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Analytical two-centre integrals in the basis set of Slater-type orbitals and explicitly correlated functions

by
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Summary

The studies of ultracold molecules, i.e. molecules cooled down to temperatures below 1 mK, constitute a new research field at the boundary of chemistry and physics. Many exciting applications of the ultracold molecules have been presented in the context of precision spectroscopy, search for physical effects beyond the Standard Model, quantum control of the chemical reactions, and many others. Most experimental studies employing the ultracold molecules require some form of theoretical support. This is true both at the stage of proposing future experiments and interpreting the existing ones. Theoretical methods employed for this purpose must fulfil a number of important requirements, e.g. they must be applicable both to light and heavy systems, and need to be reliable and accurate.

The main subject of this thesis is application of Slater-type orbitals to *ab initio* calculations on diatomic molecules which are frequently studied in the ultracold regime. Slater-type orbitals (STOs) constitute a natural basis set for expansion of the atomic and molecular wavefunctions. They originate from the exact solution of the Schrödigner equation for the hydrogen atom and possess a number of optimal analytic features, e.g. cusp at the origin and the correct long-range asymptotic decay. Therefore, one can expect a considerable gain in terms of accuracy and/or efficiency when STOs are used for expansion of the molecular orbitals. Virtually the only reason why STOs are not used routinely in quantum chemical calculations is the complicated nature of many-centre STOs matrix elements arising from the electron-electron interaction.

Development of new techniques for efficient and general calculation of these matrix elements for the diatomic systems has been the first major challenge of the present thesis. The proposed techniques have been implemented using modern programming techniques (parallelisation etc.) and tested over a wide range of parameters. This allows for routine calculations for the diatomic systems within large STOs basis set including high angular momenta ($l \leqslant 6$). Next, we have provided a general framework for design and optimisation of STOs basis sets for accurate *ab initio* calculations. Numerous benchmark calculations and comparison with the reference

data prove the validity of this scheme. Extrapolations towards the complete basis set have also been considered.

Another major goal of the present thesis has been to combine the basis set of STOs with the theory of the effective core potentials (ECPs). Effective potentials are frequently used in quantum chemical calculations, especially for heavy atoms, to eliminate a fraction of core electrons from explicit considerations and include the relativistic effects into the theoretical description. We have shown that matrix elements of ECPs within the STOs basis set can be solved with help of the Barnett-Coulson translation method. Crucially, no infinite summations appear in the final formulae. This approach has also been extended to the so-called core polarisation potentials and effective spin-orbit potentials.

To illustrate the usefulness of the methods developed in the thesis we have performed spectroscopically accurate calculations of the complete potential energy curves for two diatomic systems ($a^3\Sigma_u^+$ state of lithium dimer and the ground state of the beryllium dimer) within the basis set of STOs. In case of the Li_2 molecule the theoretically determined the spectroscopic parameters (bonding energy, equilibrium distance, vibrational energy levels, etc.) differ from the best experimental data by less than one part per thousand. The Be_2 molecule is somewhat more challenging in this context, but the obtained accuracy have allowed to confirm the existence of the weakly bound twelfth vibrational level. Subtle physical effects of relativity and quantum electrodynamics have been included in the description of both molecular systems.

Five original research papers published in international scientific journals and two (yet unpublished) preprints constitute the core of the thesis and contain a detailed account of the obtained results. The remaining unpublished results are described in a separate section of the thesis and shall be published in the near future.

Streszczenie

Ultrazimne molekuły, tj. molekuły schłodzone do temperatur poniżej 1 mK, stanowią zupełnie nowe pole badawcze na granicy chemii i fizyki. Wiele ciekawych zastosowań ultrazimnych molekuł zostało opublikowane w literaturze w kontekście dokładnej spektroskopii, poszukiwań efektów fizycznych poza Modelem Standardowym, kontroli reakcji chemicznych i wielu innych. Większość eksperymentów przeprowadzanych z użyciem zimnych molekuł wymaga pewnej formy wsparcia teoretycznego. Ta reguła stosuje się zarówno na etapie projektowania nowych eksperymentów, jak i interpretacji już istniejących. Metody teoretyczne używane w tym celu muszą spełniać szereg ważnych wymagań m.in. muszą być stosowalne do lekkich i ciężkich atomów, a także muszą być dokładne i dawać wiarygodne wyniki.

Głównym celem niniejszej pracy jest zastosowanie orbitali Slatera do obliczeń *ab initio* układów dwuatomowych, które są bardzo często badane w reżimie ultrazimnym. Orbitale Slatera stanowią naturalną bazę dla rozwinięcia funkcji falowej wieloelektronowych atomów i molekuł. Orbitale the wywodzą się z dokładnego analitycznego rozwiązania równania Schrödingera dla atomu wodoru i posiadają szereg optymalnych własności analitycznych np. ostrze w położeniu jądra i prawidłowy zanik dalekozasięgowy. W związku z tym można oczekiwać istotnych korzyści w dokładności i wydajności obliczeń jeśli orbitale Slatera zastosuje się jako bazę do rozwinięcia orbitali molekularnych. Właściwie jedynym powodem dla którego orbitale Slatera nie są stosowane rutynowo w obliczeniach kwantowo-chemicznych są trudności w obliczaniu wielocentrowych elementów macierzowych powstających jako skutek oddziaływania kulombowskiego między elektronami.

Stworzenie nowych, ogólnych technik wydajnego obliczania tych elementów macierzowych dla układów dwuatomowych jest pierwszym wyzwaniem niniejszej pracy. Zaproponowano szereg nowych metod rozwiązania tego problemu, które zostały zaprogramowane z użyciem nowoczesnych technik programistycznych (paralelizacja etc.) i przetestowane dla szerokiego zakresu występujących parametrów. Pozwoliło to wykonywać rutynowe obliczenia dla molekuł dwuatomowych w bazach orbitali Slatera zawierających wysokie momenty pędu ($l \leqslant 6$). Następnie przedstawione zostały ogólne zasady konstrukcji i optymalizacji baz Slatera przeznaczonych do ob-

liczeń *ab initio* o wysokiej dokładności. Liczne obliczenia testowe i porównania z danymi referencyjnymi dowodzą poprawności zaproponowanego schematu. Rozważone zostały również sposoby ekstrapolacji wyników do granicy bazy zupełnej.

Kolejnym ważnym celem niniejszej pracy było połączenie bazy orbitali Slatera z teorią efektywnych potencjałów rdzenia. Potencjały efektywne są szeroko stosowane w obliczeniach kwantowo-chemicznych, szczególnie dla ciężkich atomów, w celu usunięcia części elektronów rdzeniowych i wprowadzenia efektów relatywistycznych do opisu teoretycznego. Pokazano, że elementy macierzowe potencjałów efektywnych w bazie orbitali Slatera mogą być obliczane z użyciem metody przesunięć Barnetta-Coulsona. Co istotne, w końcowych wyrażeniach nie pojawiają się nieskończone sumowania. To podejście zostało zastosowane również do obliczeń z wykorzystaniem tzw. potencjałów polaryzacji rdzenia i efektywnych operatorów spin-orbita.

W celu ilustracji przydatności metod opracowanych w niniejszej pracy wykonano spektroskopowo dokładne obliczenia kompletnych krzywych energii oddziaływania dla dwóch układów molekularnych (dimer litu w stanie $a^3\Sigma_u^+$ i dimer berylu w stanie podstawowym) z wykorzystaniem baz orbitali Slatera. W przypadku cząsteczki Li_2 wyznaczone teoretycznie parametry spektroskopowe (energia wiązania, geometria równowagowa, energie poziomów wibracyjnych, etc.) różnią się od najdokładniejszych wyników doświadczalnych o mniej niż jedna część na tysiąc. Cząsteczka Be_2 stanowi trochę bardziej skomplikowany układ jednak uzyskana dokładność pozwoliła potwierdzić istnienie słabo związanego dwunastego poziomu wibracyjnego. W opisie obu układów uwzględniono subtelne efekty relatywistyczne i elektrodynamiki kwantowej.

Pięć oryginalnych artykułów badawczych opublikowanych w międzynarodowych czasopismach naukowych i dwa (jeszcze nieopublikowane) przeddruki stanowią rdzeń niniejszej pracy i zawierają dokładny opis uzyskanych wyników. Pozostałe nieopublikowane wyniki są opisane w osobnej sekcji pracy i zostaną opublikowane w bliskiej przyszłości.

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"12:45, Restate my assumptions:
1. Mathematics is the language of nature.
2. Everything around us can be represented
and understood through numbers.
3. If you graph the numbers of any system, patterns emerge.
Therefore: There are patterns everywhere in nature."

PI (1998)

Table of contents

CHAPTER 1
General introduction

1.1. The Schrödinger equation

Many scholars date the beginning of quantum chemistry back to the pioneering 1927 study of Heitler and London [1] of the hydrogen molecule. While it is very basic from today's perspective, the main results of this paper had a profound impact. It has been shown for the first time that the fundamental principles of quantum mechanics (formulated just several years before) allow for formation of a two-electron chemical bond. Despite the original results of Ref. [1] underestimated the bond strength significantly, its mere existence was startling.

The pioneering paper of Heitler and London established a completely new field of study and it is impossible to mention all related contributions from the era. However, the subsequent work of James and Coolidge [2] stands out from the rest as the first accurate theoretical description of the chemical bond in H_2. This included a systematic extension of the basis set in the spirit of Hylleraas' seminal works devoted to the helium atom [3, 4]. James and Coolidge calculated the hydrogen molecule binding energy with an error of only 0.03 eV [2]. This achievement is even more impressive if one notes that their calculations were performed mostly by hand as electronic calculators were at their infancy at that time.

A revolution in quantum chemistry came with the advent of programmable computers. This allowed to perform calculations with more flexible trial wavefunctions and approach the problem in a fully systematic way. It would be a sin to neglect the seminal contributions of Kołos here [5, 6]. He used programmable computers to find accurate wavefunctions of the hydrogen molecule. As a result, theoretical calculations surpassed the accuracy of the available experimental data - a situation unheard of in the history of molecular studies at the time. This had profound consequences - it was found that the principles of quantum mechanics not only allow for the

chemical bonding phenomenon, but also describe this process with a breathtaking accuracy.

Since the dawn of theoretical chemistry many things have changed. In particular, much larger systems can be treated routinely still retaining a reasonable accuracy and very subtle physical effects can be included in the description. There are things, however, which have not changed since the early days. One of such things is the fundamental equation which provides a starting point for many, if not most, quantum chemical methods - the Schrödinger equation [7]. It reads

$$i\hbar \frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{H}\,\Psi(\mathbf{r},t), \tag{1.1.1}$$

where $\Psi(\mathbf{r},t)$ is a time-dependent wavefunction, $\mathbf{r}$ are collective coordinates of all particles, and t is the time variable. The Hamiltonian of the system $\hat{H}$ includes kinetic energies of all particles (electrons and nuclei) and Coulomb interactions between them. In quantum chemistry one is typically concerned with stationary states, i.e. states which are eigenfunctions of the Hamiltonian and evolve with time only through a phase factor. In such situations it is sufficient to consider the time-independent Schrödinger equation

$$\hat{H}\,\Psi(\mathbf{r}) = E\,\Psi(\mathbf{r}), \tag{1.1.2}$$

where E is the total energy of the system.

The second fundamental theory in quantum chemistry is the so-called Born-Oppenheimer approximation [8, 9]. The total molecular Hamiltonian of the system in Eqs. (1.1.1) and (1.1.2) includes simultaneous motions of electrons and nuclei. However, one can intuitively feel that the nuclear motion is relatively slow, because the nuclei are much heavier than the electrons (the electron to proton mass ratio is roughly 1840). Therefore, one can attempt to uncouple these two motions by approximating the complete wavefunction of the system as a product of electronic and nuclear wavefunctions, $\Psi(\mathbf{r}) = \psi(\mathbf{r}_e;\mathbf{R})\chi(\mathbf{R})$, where $\mathbf{r}_e$ and $\mathbf{R}$ are the electronic and nuclear coordinates, respectively, so that $\mathbf{r} = \{\mathbf{r}_e, \mathbf{R}\}$. The electronic wavefunction depends only parametricaly on the nuclear coordinates. By plugging this formula into the Schrödinger equation the electronic and nuclear motions can be separated. The nuclear motion is now governed by the potential generated by the electrons. This potential is found by solving the electronic Schrödinger equation for a set of

nuclear positions

$$\hat{H}_{\mathrm{el}}\,\psi(\mathbf{r}_e;\mathbf{R}) = E_{\mathrm{el}}(\mathbf{R})\,\psi(\mathbf{r}_e;\mathbf{R}). \tag{1.1.3}$$

The electronic Hamiltonian $\hat{H}_{\mathrm{el}}$ in the atomic units is given by

$$\hat{H}_{\mathrm{el}} = -\frac{1}{2}\sum_{n}\nabla_n^2 - \sum_{n,A}\frac{Z_A}{r_{nA}} + \sum_{n<n'}\frac{1}{r_{nn'}} + \sum_{A<A'}\frac{Z_A\,Z_{A'}}{R_{AA'}}, \tag{1.1.4}$$

where n and A number the electrons and the nuclei, respectively, and r_{XY} is the distance between the particles X and Y.

If we restrict ourselves to light elements the Schrödinger equation provides a very good description of the physical reality. Even if some additional corrections are required they are typically calculated by perturbation theory. Thus, the electronic wavefunction needs to be computed beforehand anyway. Since many areas of chemistry involve mostly light elements (e.g. a significant portion of organic chemistry and biochemistry) the Schrödinger equation is a very good model in these studies. Therefore, it is not surprising that the ability to accurately solve the electronic Schrödinger equation for arbitrarily large systems is considered by many to be the quantum chemists' heaven.

1.2. Many-electron wavefunction and one-electron orbitals

The electronic Schrödinger equation is a complicated partial differential equation with many coupled variables. Exact analytical solutions are available only for several simple systems or/and some partially realistic models [10]. Moreover, purely numerical approaches to solve the many-electron Schrödinger equation have met with only a limited success thus far (e.g. basis-set-free density functional theory [11]). Therefore, it is not surprising that an overwhelming majority of quantum chemistry is based on the notion of a basis set. Instead of solving the Schrödinger equation directly for an unknown wavefunction, one expands this wavefunction in a linear combination of some predefined functions. The problem then reduces to the calculation of the optimal values of the expansion coefficients. This is fundamentally a much simpler problem known from the linear algebra.[1]

While the idea seems simple there is a problem of how to choose the expansion

[1]Parenthetically, this is also the origin for a somewhat archaic name 'algebraic approximation' referring to methods based on a finite basis set expansion [12].

functions in the general many-electron case. The conventional pick in quantum chemistry is to use the so-called Slater determinants [13]. They are antisymmetrised products of one-electron functions. The antisymmetry property is necessary because of the Pauli principle - the electrons are fermions and the wavefunction must switch sign whenever any two particles are interchanged [10]. Slater determinants can be written as

$$\phi_{\mathbf{I}}(\mathbf{r}_e) = \sqrt{N!}\,\mathcal{A}\left[\prod_{k}^{N}\varphi_{I_k}(\mathbf{x}_k)\right], \tag{1.2.1}$$

where N is the number of electrons, $\mathbf{I} = \{I_1, \ldots, I_N\}$ is a multi-index of the determinant, $\mathbf{x}_k$ stands for the coordinates (spin and spatial) of the k-th electron, and $\mathcal{A}$ is the antisymmetriser of the N-element permutational group. Due to the factor in the front the definition, Slater determinants are normalised to the unity provided that the functions $\varphi_{I_k}(\mathbf{x})$ form an orthonormal set.

One can see that Slater determinants provide a very convenient way of building fermionic many-electron wavefunctions out of a set of one-electron objects, $\varphi_m(\mathbf{x}_k)$. The latter functions (spin-orbitals) and are typically written as a product of a proper spin function (up or down) and a spatial part. Further in the thesis we refer to the spatial components as orbitals.

1.3. Criteria for a successful orbital basis

It is natural to ask the question: how to choose the orbital basis set for quantum chemical calculations within the Born-Oppenheimer approximation? How to select the functional form of the orbitals and judge its adequacy in solving the electronic Schrödinger equation? It turns out that there are at least three perspectives from which one can attempt to answer these questions.

The first is the purely mathematical approach. When the exact wavefunction is expanded into a linear combination of Slater determinants formed out of a finite set of orbitals this naturally constitutes an approximation. However, we expect that when the one-electron basis set is systematically expanded the corresponding error decreases. Finally, in the limit of infinite number of orbitals the error should vanish, i.e. the results should become exact.

Precise conditions which must be satisfied by one-electron basis set to fulfil this requirement were investigated by Kato [14], Michlin [15] and Bonitz [16] (the last

work includes also the excited states). A particularly complete answer was formulated somewhat later by Klahn and Bingel [17, 18]. Their findings can be summarised as follows. Assume that we were given an infinite set of one-electron orbitals, $\{\phi_m\}_{m=1}^{\infty}$, belonging to the Hilbert space $L^2(\mathbb{R}^3)$ of square integrable functions on the three-dimensional Cartesian space, $\mathbb{R}^3$. Let us take a finite subset of this basis, $\{\phi_m\}_{m=1}^{n}$, and form a linear combination of all possible non-redundant Slater determinants which can be assembled from this subset (denoted Φ_n). According to the variational principle [10], the optimal linear coefficients and an approximate energy can be found by minimising the Rayleigh-Ritz quotient

$$E_n = \min \frac{\langle \Phi_n | \hat{H} | \Phi_n \rangle}{\langle \Phi_n | \Phi_n \rangle}, \tag{1.3.1}$$

where $\hat{H}$ is the electronic Hamiltonian of the system. The approximations E_n converge to the exact lowest root of the Hamiltonian, i.e. $\lim_{n\to\infty} E_n = E_{\text{exact}}$, if the basis $\{\phi_m\}_{m=1}^{\infty}$ is complete[2] in the first Sobolev space[3] $W_2^{(1)}(\mathbb{R}^3)$ [19]. This is a sufficient condition for the energy convergence. It is sometimes overlooked that the completeness of the basis in the Hilbert space $L^2(\mathbb{R}^3)$ is not a sufficient criterion. Several examples of basis sets complete in $L^2(\mathbb{R}^3)$ but incomplete in $W_2^{(1)}(\mathbb{R}^3)$ are known, so this problem is of a practical interest [17, 18].

It is clear that fulfilment of the mathematical completeness criterion is a necessary prerequisite for any successful basis set. However, we are typically concerned not only with the fact that the results converge to the exact answer (albeit such property is highly appreciated), but also how fast they converge. Computational cost of any wavefunction-based quantum chemical methods scales steeply with the size of the basis set. We would like to perform calculations in basis sets as small as possible and still get satisfactory answers. The mathematical criterion outlined above says nothing about the convergence rate. A different perspective is required to say that one basis set is better than the other.

In approximating a predefined type of functions with common characteristics it is reasonable to use a basis set which is already quite close to the target. Therefore, if we know that the exact wavefunction obeys some conditions or constraints

[2] a set of functions $\{\phi_m\}_{m=1}^{\infty}$ is complete in a vector space V if any element $f \in V$ can be written as a linear combination of the elements from this set

[3] the first Sobolev space $W_2^{(1)}(\Omega)$ is a subspace of the Hilbert space $L^2(\Omega)$; by definition, a function $f \in L^2(\Omega)$ belongs to $W_2^{(1)}(\Omega)$ if $\nabla f \in L^2(\Omega)$ (differentiation is understood in the weak sense); in other words, all functions in the first Sobolev space have a finite kinetic energy

it is best to built them into our basis set explicitly. Unfortunately, the electronic Schrödinger equation is very complicated and not very much is known about the exact solution in the general case. Some properties are known, e.g. the wavefunction is square integrable, locally Lipschitz continuous[4] and has bounded first derivatives. Unfortunately, these conditions are not particularly useful. Quite amazingly, however, some very strong conditions are known to be satisfied by *any* exact solution of the electronic Schrödinger equation. The most prominent example is the Kato's cusp condition for the singlet electronic pairs [14, 20]

$$\lim_{r_{ij}\to 0}\left(\frac{\partial\Psi}{\partial r_{ij}}\right)_{av} = \mu_{ij}\, q_i\, q_j\, \Psi(r_{ij}=0) \tag{1.3.2}$$

where q_i is the charge of the particle i, μ_{ij} is the reduced mass of the particle pair i and j, and the subscript av denotes spherical averaging over an infinitesimal sphere around $r_{ij} = 0$. Many details concerning the condition (1.3.2) can be found in the paper of Pack and Byers Brown [21]. Analogous conditions for triplet electronic pairs and unnatural parity singlet pairs were also reported [21, 22].

Let us concentrate on the nuclear cusp condition, i.e. around the coalescence points of electrons with the nuclei. According to Eq. (1.3.2) the exact wavefunction in this regime is proportional to $1 - Zr$, where r is the electron-nuclear distance.[5] Moreover, the derivative of the wavefunction at the nuclei is discontinuous (hence the name - cusp condition). This condition is not simple to satisfy - basis set functions smooth around the nuclear positions struggle to reproduce this feature accurately. Therefore, significant savings can be obtained in terms of the basis set size if the cusp is built into the orbitals explicitly.

Apart from the famous cusp condition, there are some secondary conditions obeyed by the exact electronic wavefunction. For example, the wavefunction of a bound electronic state vanishes exponentially when an electron is sufficiently far away from the centre-of-mass of the molecule [23]. Higher-order cusp conditions [24–27] and many-electron cusp conditions [28–31] were also reported, but the calculated energies appear to be rather insensitive to violation of these identities [32, 33].

The third, and final, problem which must be taken into account during design

[4] a function $f : \mathbb{R} \to \mathbb{R}$ is Lipschitz continuous if there exists a constant C such that for any two points $x_1, x_2 \in \mathbb{R}$ the condition $|f(x_1) - f(x_2)| \leqslant C|x_1 - x_2|$ is satisfied; for multivariable functions the definition is analogous

[5] note that the masses of the nuclei are infinite in the Born-Oppenheimer approximation, so the reduced mass of any electron-nuclear pair is equal to the unity (in the atomic units)

and selection of the orbital basis sets is difficulty in calculation of the resulting matrix elements. In most *ab initio* quantum chemistry methods one requires several types of one- and two-electron integrals. The two-electron matrix elements are necessary to describe Coulomb interactions between the electrons and are particularly troublesome. They assume the following general form

$$\iint d\mathbf{r}_1\, d\mathbf{r}_2\; \varphi_a^*(\mathbf{r}_1)\, \varphi_b(\mathbf{r}_1)\, \frac{1}{r_{12}}\, \varphi_c^*(\mathbf{r}_2)\, \varphi_d(\mathbf{r}_2), \tag{1.3.3}$$

where $\varphi_b(\mathbf{r})$ denote the orbitals and the asterisks indicate complex conjugation. There are two main reasons why the integrals (1.3.3) require special attention. First, the integration in Eq. (1.3.3) is formally six-dimensional so a purely numerical approach is inconceivable. Preferably, one would like to have a closed-form succinct analytic expressions which can be evaluated efficiently on a computer. Second, the total number of the integrals (1.3.3) can quickly get very large. Assume that a certain one-electron basis set contains N orbitals. Then, the number of unique two-electron integrals scales as $\frac{1}{4}N^4$ for large N[6]. For basis sets larger than a couple of hundreds orbitals it is impossible to store such a massive integral files. They are typically recalculated when needed (the so-called on-the-fly or direct methods [34–37]) which gives further benefits to basis sets where robust analytic expressions for Eq. (1.3.3) are easily available.

One of significant simplifications which can be used in evaluation of the matrix elements (1.3.3) is potential existence of a product theorem. That is - a product of two orbitals (possibly located at different points of space) can be expressed in a simple closed-form. For example, a product of two Gaussian functions can be rewritten as [38, 39]

$$e^{-ar_A^2}\, e^{-br_B^2} = e^{-pr_P^2}\, e^{-ab\mathbf{AB}^2/p}, \tag{1.3.4}$$

where $p = a + b$, $\mathbf{AB} = \mathbf{A} - \mathbf{B}$, and $\mathbf{P} = (a\mathbf{A} + b\mathbf{B})/p$ is the new centre. If this relation, and its generalisation to higher angular momenta, are used under the integral sign of Eq. (1.3.3) all four-centre matrix elements are reduced to the two-centre ones. Moreover, the latter can be evaluated analytically as first shown by Boys [38, 39]. This is the main reason for the widespread popularity of the Gaussian-type orbitals (GTOs) as a basis set in quantum chemistry. This practical advantage of GTOs trumps its obvious drawbacks such as fundamental inability to satisfy the cusp

[6] for purely real orbitals this number is reduced twice to $\frac{1}{8}N^4$

condition or wrong long-range asymptotic behaviour. This illustrates how important the practical considerations are in development of successful basis sets.

1.4. Exponential-type orbitals

Let us introduce a class of exponential-type orbitals which are the main subject of the present thesis. They originate from analysis of the well-known exact solution of the electronic Schrödinger equation for the hydrogen-like atoms without external fields [10]. In the atomic units the solution for the bound states reads

$$\psi_{nlm}(\mathbf{r}) = \left(\frac{2Z}{n}\right)^{3/2} \sqrt{\frac{(n-l-1)!}{2n\,(n+l)!}} \rho^{\,l}\, L^{2l+1}_{n-l-1}(\rho)\, e^{-\rho/2}\, Y_{lm}(\theta,\phi), \tag{1.4.1}$$

where Y_{lm} are the spherical harmonics in the Condon-Shortley phase convention, $\rho = 2Zr/n$, L^{2l+1}_{n-l-1} are the associated Laguerre polynomials, and Z is the nuclear charge. The three quantum numbers n, l, m are integers subject to conditions $n > 0$, $l < n$, and $-l \leqslant m \leqslant l$.

One can see that the functions (1.4.1) fundamentally consist of a polynomial times a simple exponential. This feature defines the broad class of exponential-type basis sets (or exponential type orbitals). Obviously, there is a large freedom in choosing the actual functional form and various exponential-type basis sets were proposed in the literature. Some of them are described and analysed in the further sections of the thesis. Here, we are concerned mostly with the Slater-type orbitals (STOs) introduced as early as 1928 by Slater in his pioneering works on many-electron atoms [13, 40, 41]. The definition of STOs is appealingly simple and transparent

$$\chi_{nlm}(\mathbf{r};\zeta) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}}\, r^{n-1} e^{-\zeta r}\, Y_{lm}(\theta,\phi), \tag{1.4.2}$$

where ζ is a (positive) nonlinear parameter, $n > l$, and the factor in front of the definition is the normalisation constant. The initial idea of Slater was that the value of ζ reflects the effective charge which is experienced by an electron on a given orbital. For further use we additionally would like to introduce the so-called canonical STOs. They are formally given by the expression (1.4.2) but the value of n is fixed to $l+1$. The use of canonical STOs has certain practical advantages which are explained further in the thesis.

Based on the results of the previous section we can judge the adequacy of STOs as a basis set for quantum chemical calculations. First, the mathematical criterion of completeness is satisfied provided that the parameters ζ are chosen properly [18]. More precisely, the basis set $r^l e^{-\zeta_{ml} r} Y_{lm}(\theta, \phi)$ is complete in $W_2^{(1)}(\mathbb{R}^3)$ if for each $l = 0, 1, 2, \ldots$ the positive real sequence $\{\zeta_{ml}\}_{m=1}^{\infty}$ has an accumulation point[7]. As outlined in the previous section, this guarantees that the variational calculations are convergent to the exact result.

Let us now pass to the analytic properties which are expected from a "good" basis set. This is also where the Slater-type orbitals excel. Provided that the values of ζ are chosen reasonably, STOs are able to satisfy the nuclear cusp condition, i.e. they naturally encompass the derivative discontinuity of the exact wavefunction at the nuclear positions. This suggests that a relatively small basis set of STOs can faithfully describe electronic density in vicinity of the nuclei. This is a crucial merit in accurate calculations of various important quantities such as relativistic effects, core-valence correlations, and many related properties. Moreover, the exponential decay of the exact electronic density can also be correctly described eliminating unphysical artefacts in the calculations of (hyper-)polarisabilities, long-range van der Waals constants, etc. Overall, a basis set composed of STOs can be expected to give noticeably better results than GTOs basis set of the same size. This effect should not be understated, especially in face of steep scaling of the computational costs in accurate quantum chemistry methods.

One may wonder why the Slater-type orbitals are not frequently used in accurate molecular *ab initio* calculations if their properties are so superior in comparison with the widely employed GTOs. The answer lies in difficulties in calculation of the matrix elements (1.3.3). There is no simple product theorem for STOs - a product of two STOs located at different points of space is *not* an STOs, but rather a complicated bi-centric function. Nonetheless, a distant analogue of Eq. (1.3.4) can be found in the literature [42]. It reads

$$\frac{e^{-\zeta_a r_A}}{r_A} \frac{e^{-\zeta_b r_B}}{r_B} = \frac{1}{\pi} \int_0^1 du \, \frac{\zeta_u^2}{[u(1-u)]^{3/2}} \hat{k}_{-1} \left(\zeta_u \sqrt{R^2 + \frac{r_u^2}{u(1-u)}} \right), \tag{1.4.3}$$

where $\hat{k}_{-1}(z) = \frac{1}{z} K_{-1}(z)$ and K_ν is the modified Bessel function of the second kind,

[7] we say that a sequence $(a_n)_{n=1}^{\infty}$ has an accumulation point a if one can find a subsequence $(a_{n_k})_{k=1}^{\infty}$ such that for each $\epsilon > 0$ there exists a value of K such that for $k > K$ we have $|a_{n_k} - a| < \epsilon$. If a sequence has a finite limit then it is the only accumulation point of this sequence.

$\mathbf{r}_u = \mathbf{r} + u\mathbf{R}$, $\mathbf{R} = \mathbf{B} - \mathbf{A}$, and $\zeta_u = \sqrt{\zeta_a^2 + \zeta_b^2\,(1-u)}$. One can say that the root of all difficulties in treatment of STOs matrix elements can be (at least partially) attributed to the impracticality of Eq. (1.4.3).

1.5. Motivation and context of the thesis

It may not be a well-known fact that studies of diatomic molecules constitute an important niche at the boundary of chemistry and physics and an active field of current research. This is especially true in the context of the so-called ultracold chemistry and physics. In fact, a considerable interest in molecules cooled down to very low temperatures was sparked by magnificent advances in use of magnetic and electromagnetic control techniques to assemble cold (<1 K) and ultracold (<1 mK) molecules directly from the corresponding atoms. One of the most fascinating aspects of the (ultra)cold regime is how different it is from the world that chemists study on a daily basis. In particular, quantum nature of all processes is blatantly visible. This gives rise to superconductivity, superfluidity, Bose-Einstein condensation and other puzzling phenomena. Because our interest in the ultracold chemistry is one of the main motivations for undertaking this work, a more in-depth introduction to the this topic is appropriate.

The beginning of the ultracold physics can be dated back to 1995 when Bose-Einstein condensation of atomic gases has been achieved for the first time [43, 44]. This effect was predicted theoretically a long time ago [45, 46] but was notoriously difficult to realise under experimental conditions. In fact, Bose-Einstein condensate - a quantum phase comprised of many bosons occupying the ground state of the system - can be obtained only if the thermal de Broglie wavelength of the particles is comparable to their average spacial spacing. Back-of-the-envelope calculations predict that atoms need to be cooled to a tiny fraction of a Kelvin to create such conditions. This major problem was finally resolved by means of the so-called laser cooling techniques [47–51]. Since then, Bose-Einstein condensation has been achieved for many elements including the alkaline atoms (lithium [52, 53], sodium [44, 54], potassium [55, 56], rubidium [43], caesium [57]), alkaline earth metals (calcium [58], strontium [59–61]), lanthanide atoms (ytterbium [62–64], dysprosium [65]) and some others [66, 67]. Quite recently, Bose-Einstein condensate of the hydrogen atoms has been created by means of evaporative cooling [68].

In contrast with atoms, laser cooling techniques are not applicable to molecules.

This is mostly due to the presence of numerous rotational and vibrational states which complicate the structure of the energy levels. There are only a handful of exceptions from this rule [69, 70]. Therefore, completely new techniques were developed to bring molecules to low temperatures. They can be divided into two types. Direct methods concentrate on cooling stable molecules which are synthesised beforehand (e.g. buffer gas colling [71, 72], Stark and Zeeman deceleration [73, 74]). Indirect methods attempt to form molecules from atoms which have already been cooled with suitable techniques. This class includes photoassociation [75] and magnetoassociation [76] as prime examples. To date, many molecules have been cooled to ultralow temperatures, both with direct (e.g. CO [73], LiH [77], NH [78], OH [79], H_2CO [80], YbF [81], CaH [71], CaF [82]) and indirect techniques (e.g. LiCs [83], KRb [84], Sr_2 [85], Cs_2 [86]), but it is impossible to mention all important contributions here. Note that most of these molecules are diatomic species.

It might not be clear yet what exactly the ultracold molecules have to offer in comparison with the already well-established field of the ultracold atoms. First, molecules have a larger number of internal degrees of freedom due to rich vibrational and rotational structure. This introduces into considerations completely new energy scales. Second, many molecules have permanent electric and/or magnetic dipole moments which allows to control and manipulate them with help of external fields. Let us present several examples of current and future applications where these advantages are exploited.

Probably the most numerous and highly regarded applications of the ultracold molecules are in the field of precision spectroscopy. Note that at ultralow temperatures the molecules can be prepared virtually in a single quantum state. Moreover, various perturbations present at higher temperatures are almost entirely eliminated. All these factors contribute to highly increased precision of the measurements, impossible to achieve by other means. In particular, cold molecules are suitable for spectroscopy of very weakly bound levels lying close to the dissociation limit [87–89]. These levels are sensitive to physical effects which are ordinarily extremely tiny (relativistic, adiabatic or QED contributions) [90, 91, 93]. For the sodium dimer it was necessary to include very subtle effects of retardation of the electromagnetic radiation to correctly reproduce the experimental data [92]. Similarly, weakly bound levels of Sr_2 are sensitive to nonadiabatic couplings between electronic states [94, 95]. Such measurements have an additional benefit of providing rigorous benchmarks for the available theoretical models.

The impressive accuracy attainable in the measurements in the ultracold regime has other uses. The results have been employed in various studies of physical effects beyond the Standard Model. For example, high-resolution data obtained for OH [96], CH [97] and CO [98] molecules was used to calculate upper bounds for the time variation of the fine-structure constant, α. Similarly, ultracold Cs_2 [99], Sr_2 [100], CaH^+ [101], and MgH [102] provide constraints on the proton to electron mass ratio variations. Molecules YbF and SrF were used to study the possibility of parity violations and give upper bounds on the permanent electric dipole moment of the electron [103, 104]. Clearly, all these studies touch the very fundamentals of our state of knowledge.

Another interesting problem is the observation and control of chemical reactions at ultralow temperatures. It turns out that due to the so-called resonance enhancement chemical reactions can occur at surprisingly high rates in this regime. This was observed for reactions of alkali-metal atoms [105, 106] (Cs_2+Cs and Na_2+Na) but also for a more conventional proton exchange process, F+H_2 →HF+H [107, 108]. Moreover, it was reported that reaction rates can be effectively controlled by applying external fields [109–113]. A similar effect can be observed when the nuclear spin states of the interacting species are manipulated [114]. Therefore, ultracold molecules provide an important proving ground for the theory of quantum control of chemical reactions.

We must stress that *ab initio* calculations of the electronic structure and the corresponding nuclear dynamics play a crucial role in the studies of the ultracold molecules. A substantial theoretical input is required to propose future experiments and interpret the existing ones. In particular, forward knowledge of the electronic structure can be obtained only from the theoretical calculations or from earlier experiments. The latter are usually not available or very old. Within the present state of the electronic structure theory many key elements such as interaction potentials, transition dipole moments, spin-orbit and non-adiabatic couplings, polarisabilities, long-range interaction asymptotic coefficients etc. can be calculated from first principles. To appreciate the importance of theoretical calculations in studies of ultracold molecules we would like to point out the recent review papers of Krems [110, 115], Carr et. al. [116], Quéméner and Julienne [117], and Balakrishnan [118]. They touch upon various aspects of the theory necessary to describe the chemistry and physics of the ultracold regime. However, this is only the tip of the iceberg.

Let us conclude the present section with a few remarks. First, what traits a

quantum chemistry method must have to be useful in applications to the ultracold molecules? Probably the first thing that comes to mind is the accuracy. As pointed out numerous times before, the present day measurements in the ultracold regime reach an unprecedented accuracy. Understandably, the theory has to keep up with this progress. This favours *ab initio* methods which provide consistent and reliable results and, preferably, allow for estimation of the residual errors. Second, many molecules mentioned above are comprised of heavy atoms. As it is well-known, relativistic effects (and possibly also the QED and retardation effects) play crucial role in the electronic structure of such systems and cannot be neglected in accurate studies. Fulfilment of these high requirements is a constant challenge for the state-of-the-art first-principles methods.

1.6. Objectives of the thesis

The primary objectives of the thesis are the following:

- to develop new techniques for the calculation of standard one- and two-electron matrix elements over STOs guaranteeing sufficient accuracy and stability for use in precision studies; to efficiently implement the new formulae using modern programming techniques (parallelisation etc.) and test them over a wide range of parameters,

- to present a general framework for design and optimisation of STOs basis sets for accurate *ab initio* calculations; perform necessary benchmark calculations and compare with the reference data; test the reliability of extrapolations towards the complete basis set limit; check the adequacy of the new basis sets for the calculation of relativistic and other effects beyond the nonrelativistic Born-Oppenheimer approximation,

- to develop methods for the evaluation of STOs matrix elements of various operators necessary to compute a range of important quantities such as the permanent and transition electric multipole moments, nonadiabatic and spin-orbit coupling matrix elements, leading-order relativistic corrections, etc.,

- to combine the basis set of STOs with the effective core potentials (ECPs) approximation thereby opening the window for applications of STOs to heavy elements; this includes also the so-called core polarisation potentials and effective spin-orbit potentials,

- as the first application to many-electron systems to perform state-of-the-art theoretical calculations for the $a^3\Sigma_u^+$ state of the lithium dimer with the basis set of STOs and compute the complete potential energy curve for this system; theoretically determine the spectroscopic parameters (binding energy, equilibrium distance, vibrational energy levels, etc.) and compare with the best available experimental data; determine the scattering length of two lithium atoms in the ground state from the purely *ab initio* data,

- as the second test to calculate the complete potential energy curve for the ground state of the beryllium dimer including the relativistic, adiabatic, and QED effects; investigate the relative importance of various QED contributions to the interaction energy; determine the theoretical vibrational energy terms and confirm or deny the existence of the weakly bound twelfth vibrational level; compare the results with the data obtained by using (semi-)empirical potentials.

1.7. Structure and organisation of the thesis

This thesis is organised into five main Chapters, two Appendices, and a bibliography. The first Chapter provides a general introduction. It puts the present research into a broader context, justifies the motivation for carrying out this study, stresses its importance and potential applications. The second Chapter is an extensive survey of the literature, describing the existing methods for the calculation of STOs matrix elements, their strengths and weaknesses. The third Chapter gathers the main results of the study - five original research articles published in international peer-reviewed journals and two preprints (unpublished yet). Further in the thesis we refer to them as Papers I-VII. Every article is preceded by a commentary (an extended abstract) which allows for a better understanding of the contributions contained in each paper and links them together. The fourth Chapter presents various unpublished results and methods developed in the course of the work. Every section of this chapter is preceded by a short commentary where reasons for considering each problem are reviewed. If necessary, the most important literature references are given. The fifth Chapter summarises the present work, gives the final conclusions and an outlook for the future. Finally, Appendices provide some details concerning the present study which are too technical to fit into the main text, but are nonetheless important. At the very end of the thesis a complete bibliography is given. Atomic

units ($m_e = e = \hbar = 1$, etc.) are used throughout the thesis unless explicitly stated otherwise.

CHAPTER 2

Literature survey

In this section we provide an extensive survey of the literature devoted to the Slater-type orbitals and summarise the most important developments in the field published prior to the completion of the thesis. Despite several reviews of this broad topic are available in the literature [119, 120] we believe that this gentle introduction may be necessary to better understand the context of the present thesis as well as its impact and importance. The presentation is not given in the chronological order - we do not attempt to provide a historical perspective. This is mostly because some methods proposed in the literature back in the day appeared to be very promising, but are almost obsoleted by today's standards. Instead, we concentrate on the most prolific and impactful classes of methods for the calculation of the matrix elements with Slater-type orbitals. The biggest emphasis is put on methods which were used in Papers I-V or which provided a major inspiration for the present work. Additionally, two types of methods were excluded from the review. First, we neglected all schemes which are not general, e.g. valid only for orbitals with a limited angular momentum. Second, we do not discuss methods which are purely numerical such as in the ADF program package [121–123]. Despite these methods are impressive in terms of the efficiency and are applicable to polyatomic molecules, they impose some further approximations in computation of the matrix elements, e.g. density fitting. While this pragmatic approach is certainly justified in the density functional theory calculations where the so-called chemical accuracy (≈ 1 kcal/mol) is desired, they do not fulfil the spectroscopic accuracy standards of the present work. Lastly, this survey concentrates on methods devoted to diatomic molecules.

2.1. Translation methods

As the name suggests, this broad class of methods aims to shift STOs from one point of space to another. More specifically, the goal is to express a single STO placed at a certain point of space as a series expansion involving quantities located at a different centre only. The main idea behind the translation methods is simple: if all orbitals present in the matrix elements can be expanded around a common centre then we are left with a simpler one-centre integral (i.e. atomic integral). Integration over the angles in the spherical coordinate system is typically relatively straightforward, leaving only a one-dimensional radial integral. This is why the translation methods are sometimes called "the single-centre expansions". These two names shall be used interchangeably further in the text. The translation techniques can be further subdivided into two main categories: one-range and two-range expansions.

The one-range expansions result from simple concepts of the Hilbert space theory. STOs centred at an arbitrary point of space $\mathbf{R}$ can be written as $\chi_{nlm}(\mathbf{r}-\mathbf{R})$. Let us take an orthonormal set of functions $\varphi_n^w(\mathbf{r})$ complete in $L_w^2(\mathbb{R}^3)$, where $w(\mathbf{r}) > 0$ is a weight function, with the inner product is defined as $\int d\mathbf{r}\, w(\mathbf{r}) \left[f(\mathbf{r})\right]^* g(\mathbf{r})$. The weight function must be chosen carefully so that $\chi_{nlm}(\mathbf{r}-\mathbf{R}) \in L_w^2(\mathbb{R}^3)$. The fundamental principles of the Hilbert space theory tell us that we can write

$$\chi_{nlm}(\mathbf{r}-\mathbf{R}) = \sum_n \varphi_n^w(\mathbf{r}) \int d\mathbf{r}\, w(\mathbf{r}) \left[\varphi_n^w(\mathbf{r})\right]^* \chi_{nlm}(\mathbf{r}-\mathbf{R}), \tag{2.1.1}$$

which is the exact relation, not an approximation. Therefore, the function centred at $\mathbf{R}$ $\chi_{nlm}(\mathbf{r}-\mathbf{R})$ has been expressed in terms of $\varphi_n^w(\mathbf{r})$ which are located at the origin. The coefficients of this expansion are simple overlap integrals between the translated function and the adopted basis. Note that there is a significant freedom of choice in the one-range formulation. First, we are free to select any $w(\mathbf{r})$ as long as STOs belong to the corresponding Hilbert space. Second, one can select any orthonormal basis set $\varphi_n^w(\mathbf{r})$ from $L_w^2(\mathbb{R}^3)$ and obtain fully equivalent results.

The appealing nature of the one-range translation methods was probably first realised by Smeyers [124, 125]. A simple hydrogen-like basis set was originally used for the expansion (2.1.1). Later, many more modifications and improvements were introduced with notable contributions from Filter and Steinborn [126, 127], Fernández Rico et al. [128–130], Guseinov [131, 132] and others [133–135]. However, major limitations of this expansion were first pointed out by Trivedi and Steinborn [136] who

showed that a very large number of terms is necessary to achieve convergence. This makes calculation of the expansion coefficients very problematic. An amazingly large number of papers concerning the one-range expansions were published by Guseinov and collaborators, see Refs. [137–146] as representative examples. Unfortunately, the mathematical validity of some aspects of the Guseinov one-range expansions has recently been questioned in a series of papers by Weniger [147–149]. This appears to be a controversial topic and we do not want to discuss it any further here.

The two-range expansions are more complicated in nature. The founding example of such expansion is the famous Laplace expansion of the Coulomb potential. More generally, if we have a function $f(\mathbf{r}-\mathbf{r}')$ dependent on coordinates of two particles then the corresponding two-range expansion is expressible through $r_< = \min(r, r')$ and $r_> = \max(r, r')$. In other words, the functional form of a two-range expansion depends on the relative location of the particles. There is a substantial mathematical difference between the one-range and two-range expansions. The former are typically convergent only in the mean, i.e. with respect to the norm of the corresponding Hilbert space, while the latter are convergent pointwise almost everywhere, i.e. whenever $r \neq r'$.

The two fundamental two-range translation methods for STOs are the Barnett-Coulson ζ-function [150–152] and Löwdin α-function [153] techniques. Since these approaches are very closely related we concentrate on the former here. It can be traced back to the following relation

$$r_b^{n-1} e^{-\beta r_b} = \sum_{m=0}^{\infty} \frac{2k+1}{2} P_m(\cos\theta_a)\, \zeta_{nm}(\beta, r_a; R), \tag{2.1.2}$$

where P_m are the Legendre polynomials, R is the distance between centres, and ζ_{nm} is explicitly defined in Paper V. It may not be immediately obvious why this expansion belongs to the two-range class. The reason is that the function ζ_{nm} is given by different formulae in the manifolds $r_a > r_b$ and $r_a < r_b$.

Sometime after the introduction the Barnett-Coulson method has been generalised to arbitrary quantum numbers [154, 155]. Since then it has been applied to calculation of a plethora of matrix elements involving STOs. This includes, but is not limited to, multicentre electron repulsion integrals of various types [156–165], nuclear repulsion integrals [166–171], overlap and related integrals [172–177], and many others. In some of the aforementioned examples the Barnett-Coulson method was combined with other techniques to boost the overall performance or to sim-

plify the resulting algorithms. Additionally, many alternative two-range translation formulae were put forward in the literature, cf. Ref. [178–189] and references therein. Some of them involve only convenient rearrangements of terms in the working expressions, but others are fundamentally new relations offering some theoretical or practical advantages. To sum up, two-range translation formulae (in various forms) were extremely popular at the time, and were widely considered to be the most promising tools in solving the notoriously difficult matrix elements, especially in the polyatomic molecules. For example, the first versions of the STOP program package of Hoggan and collaborators [190] were based almost exclusively on various single-centre expansions.

The biggest problem of the two-range addition theorems is that they lead, in general, to infinite expansions which have to be truncated for practical reasons. In some cases one obtains several infinite summations in one working expression. To address this issue many authors studied convergence properties of the series resulting from the application of the Barnett-Coulson and related methods [191–195]. Unfortunately, pathologically slow convergence was observed in many cases where thousands of terms were necessary to achieve any reasonable precision. Moreover, the convergence rate was highly dependent upon the values of the nonlinear parameters and/or quantum numbers. The computational cost of lengthy infinite summations (and other practical considerations) rule out this method as a serious alternative in such cases. To circumvent this obstacle numerous acceleration techniques were put forward [196–199]. However, it appears to be a very difficult task to devise an acceleration scheme which behaves reasonably well over a wide range of parameters typically encountered. To the best of our knowledge, this problem has not found a satisfactory solution yet.

2.2. Gaussian expansion and Gaussian transform methods

In this section we discuss various methods which aim to transform matrix elements over STOs into similar expressions involving Gaussian functions only. This class of methods can be divided into Gaussian expansion and Gaussian transform techniques. The former rely on the fact that STOs can be approximated with an arbitrary accuracy by a properly tailored linear combination of GTOs. Interest in this technique was sparked by the famous papers of Boys and collaborators [38, 39] who showed that the electron repulsion integrals over GTOs can be reduced to a

simple one-dimensional integration with relative ease. The latter integral is closely related to the incomplete Gamma function and is usually called the Boys function [200–203]. Therefore, if all STOs present in the matrix elements are expanded into a linear combination of GTOs the resulting expression can be evaluated analytically. This prompted development of the so-called STO-nG basis sets [204–207] with varying length of the expansion, n. Due to the simplicity and robustness of the Gaussian expansion method it has been used very frequently. For example, this was the main method to calculate the two-electron integrals in the first versions of the SMILES program package [208, 209]. However, it is not difficult to realise the drawbacks of the discussed method. To reach high accuracy of the calculation one needs very long expansions. The cost of the computations scales as the fourth power of the expansion length and thus becomes prohibitive rather quickly, especially when high angular momentum functions come into play. Our experience shows that it is also very difficult to systematically increase the accuracy due to numerical round-off errors accumulation [210–212]. In the present work the Gaussian expansion method is applied only for a few classes of integrals which are very difficult to compute analytically within the STOs basis. Fortunately, the accuracy of several significant digits is entirely sufficient in such cases (e.g. two-electron relativistic effects, see Papers VI-VII).

The Gaussian transform method can be viewed as a continuous analogue of the Gaussian expansion discussed above. It relies on integral transformations which allow to rewrite the exponential function as a Gaussian function at a cost of additional one-dimensional integration. The original transformation formula due to Shavitt and Karplus [213–216] reads

$$e^{-\alpha r} = \frac{\alpha}{2\sqrt{\pi}} \int_0^\infty \frac{ds}{s^{3/2}}\, e^{-\alpha^2/4s}\, e^{-sr^2}, \tag{2.2.1}$$

which can be viewed as a particular form of the Laplace transform. A straightforward application of this formula allows to reduce the six-dimensional integrations present in the usual two-electron integrals to four-dimensional integrations. Unfortunately, calculation of the remaining integrals is still non-trivial and has to be accomplished numerically (at least partially). Moreover, the transformation formula (2.2.1) is very convenient for ns orbitals but becomes much more cumbersome for higher angular momenta.

The Gauss transform method has been progressively refined over many years.

The main improvements were due to more robust integral transforms [217–219], applications to various matrix elements [220–226], generalisations to higher angular momenta [174, 227], combinations with efficient numerical quadratures [189], and others [228–230]. A combination of Gaussian transforms with the so-called shift method (discussed further) is also very promising. It appears that the most problematic aspect of the methods relying on the integral transformations is their high computational cost, mostly due to multidimensional numerical integrations.

2.3. Methods based on the ellipsoidal coordinates

The ellipsoidal coordinates (otherwise known as prolate spheroidal coordinates) are curvilinear coordinates frequently used in studies of systems with axial (i.e. cylindrical) symmetry. To specify this coordinate system one has to choose two points in space, further denoted a and b, lying on the z axis (by convention). The ellipsoidal coordinates ξ, η and ϕ are then defined as

$$\xi = \frac{r_a + r_b}{R}, \quad \eta = \frac{r_a - r_b}{R}, \quad \phi = \operatorname{arc\,tg} \frac{y}{x}, \tag{2.3.1}$$

where r_a and r_b denote distances to the centre a and b, respectively. The volume element in these coordinates reads $\left(\frac{R}{2}\right)^2 (\xi^2 - \eta^2)$. It seems obvious that the ellipsoidal coordinates are ideal for studying diatomic molecules. Let us mention, however, that they were introduced long before the discovery of quantum mechanics as a set of coordinates where complete separation of variables in the classical Laplace equation is possible. To this day, the ellipsoidal coordinate system is used in many areas of electrostatics, classical mechanics etc.

The usefulness of the ellipsoidal coordinate system in the calculations of molecular integrals involving STOs has been realised very early - the famous paper of James and Coolidge [2] is the prime example. Systematic methods for the calculation of the overlap integrals within STOs basis based on the ellipsoidal coordinates were pioneered by Mulliken et al. [231] and subsequently improved by Corbató [232] and by Harris [233]. Many authors extended this method to the calculation of other one-electron integrals [172, 234–237], including cases as difficult as the general three-centre nuclear attraction integrals [238–241]. It was also realised that methods based on the ellipsoidal coordinates possess considerable advantages in the evaluation of the electron repulsion integrals. This is mostly due to the existence of the Neumann expansion which is, in substance, a two-range two-centre expansion of the Coulomb

potential in terms of ξ, η, and ϕ. It reads

$$\frac{1}{r_{12}} = \frac{2}{R}\sum_{\mu=0}^{\infty}\sum_{\sigma=-\mu}^{\mu}(-1)^{\sigma}(2\mu+1)\left[\frac{(\mu-|\sigma|)!}{(\mu+|\sigma|)!}\right]^2 \times P_{\mu}^{|\sigma|}(\xi_<)Q_{\mu}^{|\sigma|}(\xi_>)P_{\mu}^{|\sigma|}(\eta_1)P_{\mu}^{|\sigma|}(\eta_2)e^{i\sigma(\phi_1-\phi_2)}, \tag{2.3.2}$$

where $\xi_< = \min(\xi_1, \xi_2)$, $\xi_> = \max(\xi_1, \xi_2)$, and the remaining quantities were defined in Papers I and II. Interestingly, extensions of the Neumann expansion to higher powers of the interelectronic distance [242, 243] and other forms of the interaction operator were presented [244–249], along with several other modifications [250, 251]. The first application of the Neumann expansion to general two-centre two-electron integrals over STOs dates back to the series of papers by Ruedenberg and collaborators [252–255]. This led to tabulation of some basic electron repulsion integrals in the books of Kotani [256], Roothaan [257, 258], and Preuss [259]. In the late 50' and 60' many authors contributed to the development of the theory, improving it both in terms of accuracy and speed [191, 192, 260–265]. Unfortunately, it seems that after these pioneering achievements the progress stalled somewhat. The number of papers devoted to the calculation of the molecular integrals with help of the Neumann expansion (or ellipsoidal coordinates in general) dropped considerably. Throughout the 70' only a few significant contributions to the field were published [266–268]. This can probably be (at least partly) attributed to the growing popularity of the Gaussian-type orbitals and development of codes capable of handling arbitrary polyatomic molecules. The impasse was broken in early 90' when interest in methods based on the Neumann expansion rejuvenated [269–274] and continues to this day. In particular, the paper of Maslen and Trefry [271] was very innovative. The authors recognised some of the most difficult integrals appearing in the theory in terms of known special functions. This allowed to propose new methods for evaluation, partly free of the numerical problems characteristic for the previous approaches. This idea was further refined by Harris in his 2002 paper [273]. We must note that these two works were the major inspiration for the analytic approach developed in Paper II of this thesis.

To finalise this section we comment shortly on the convergence characteristics and applicability of the Neumann expansion. Due to its two-range form it can be shown to be pointwise convergent almost everywhere. This is a very strong condition - sufficient to guarantee convergence of all electron repulsion integrals whenever Eq. (2.3.2) is inserted instead of $\frac{1}{r_{12}}$ under the integral sign. In fact, a weaker condition

of convergence in the mean would also suffice. Therefore, methods based on the Neumann expansion are completely general in the sense that all physically acceptable combinations of the exponents and quantum numbers lead to convergent expressions. Unfortunately, some authors confused the convergence property of the Neumann expansion with the ability to calculate the higher-order terms accurately [195]. If some of the terms in the series are calculated with insufficient precision one can observe an apparent divergence. However, this is always an indication of the digital erosion (or other technical problems), not a problem with the Neumann expansion itself.

2.4. Methods involving Coulomb Sturmians

The basis set of Coulomb Sturmians was originally introduced by Shull and Löwdin [275] as a solution of the following scaled one-electron Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + \frac{1}{2}k^2 - \frac{nk}{r}\right]\chi_{nlm}(\mathbf{r}) = 0, \tag{2.4.1}$$

where $k > 0$, subject to the potential-weighted orthogonality relation

$$\int d\mathbf{r}\, \chi^*_{nlm}(\mathbf{r})\, \frac{1}{r}\, \chi_{n'l'm'}(\mathbf{r}) = \frac{k}{n}\, \delta_{nn'}\, \delta_{ll'}\, \delta_{mm'}. \tag{2.4.2}$$

One of the advantages of the Sturmians is that they form a discrete and complete set for any fixed k (cf. Refs. [276–278] and references therein). Note that this is not true for the bound solutions of the Schrödinger equation for the hydrogen atom (i.e. without the continuum states). Since they introduction, Coulomb Sturmians have been applied to a multitude of problems in atomic physics, especially for few-body systems (see Refs. [279–283] as representative examples). It is then a natural question whether the Sturmians can used in calculations for molecular systems. Pioneering steps in this direction were reported by Shibuya and Wulfman [284], Aquilanti and collaborators [285, 277, 286, 287], and Koga and co-workers [289, 290]. As a byproduct, interesting relationships between the Sturmian basis and the theory of hyperspherical harmonics [291] were found. Some extensions of the Sturmian orbitals were also proposed [292]. Many important contributions to the field came from the group of Avery with applications to simple two-centre systems already available [293–301].

The biggest problem of the Coulomb Sturmians is the fact they include only one length scale in the basis set. In other words, all functions share the same exponent, k. This is acceptable in the calculations of the atomic spectra where many processes can be modelled by a small number of (active) valence electrons experiencing some effective (screened) nuclear charge. On the other hand, in many-electron molecules several length scales appear almost naturally and importance of different length scales is highly dependent on the molecular geometry. Therefore, one can expect a slow convergence of the results with respect to the size of the basis. Unfortunately, simplicity and elegance of the Coulomb Sturmians basis relies heavily on the assumption of a single exponent. It seems that extensions to many length scales would negate these advantages.

2.5. The shift method and related techniques

The shift method has been introduced rather recently by Fernández Rico and coworkers [302]. It draws some inspiration from the methods designed for calculation of the molecular integrals over Gaussian-type orbitals, in particular from the McMurchie-Davidson scheme [303, 304]. The main idea is to explicitly calculate only the simplest (basic) integrals involving pairs of χ_{000} functions. Higher angular momenta in the orbitals are subsequently generated by action of a differential operator (shift operator) on this basic analytic expression. Construction of a proper operator was probably first considered by Shavitt and Karplus [215] in the spherical coordinates representation and by Wright [305] in the Cartesian representation of the orbitals. However, these initial applications led to very complicated and non-transparent formulae. A more elegant procedure was devised by Weniger and Steinborn [306], but it was applicable only in the context of the B-functions. Fernández Rico and coworkers [302] proposed the following formula for purely real (and unnormalised) STOs

$$\chi_{nlm}(\mathbf{r}_a;\zeta) = \Omega^n_{lm}(a)\,\frac{e^{-\zeta_a r_a}}{r_a}. \tag{2.5.1}$$

The shift operator is given by

$$\Omega^n_{lm}(a) = \hat{\mathcal{Z}}_{lm}\left(\nabla_a\right)\left(-\frac{\partial}{\partial\zeta_a}\right)^{n-l}\left(-\frac{1}{\zeta_a}\frac{\partial}{\partial\zeta_a}\right)^{l}, \tag{2.5.2}$$

where ∇_a denotes the gradient operator acting on the coordinates of the nucleus a, and $\hat{\mathcal{Z}}_{lm}(\nabla)$ are the (real) spherical tensor gradient operators. The latter quantities can heuristically be obtained by taking the formula for the real solid spherical harmonics (in the Cartesian representation) and replacing all coordinates x, y, z by the corresponding differentials ∂_x, ∂_y, ∂_z. A detailed and impressively complete discussion of the properties of $\hat{\mathcal{Z}}(\nabla)$ can be found in the recent monography of Weniger [307]. Pioneering results on this topic in the quantum-chemical context were published by Dunlap [308].

Some comments on the properties of Eqs. (2.5.1) and (2.5.2) are necessary. First, note that the order of differentiation in Eq. (2.5.2) is important because the operators ∂_ζ and $\zeta^{-1}\partial_\zeta$ do not commute. Second, the use of spherical tensor gradient operators is particularly convenient, mostly due to their superior mathematical properties. For example, the action of $\hat{\mathcal{Z}}(\nabla)$ on a function which depends solely on the radial coordinate can be resolved easily as

$$\hat{\mathcal{Z}}(\nabla)\, f(r) = \mathcal{Z}_{lm}(\mathbf{r}) \left(\frac{1}{r}\frac{\partial}{\partial r}\right)^l f, \tag{2.5.3}$$

where $\mathcal{Z}_{lm}(\mathbf{r})$ are the solid spherical harmonics (in the real form). Parenthetically, this is a special case of the Hobson theorem [309, 310], cf. Ref. [307].

As a simple example, we apply the shift method to the two-centre overlap integrals over STOs. By recalling Eqs. (2.5.1) and (2.5.2) one can write

$$\begin{aligned}\int d\mathbf{r}\, \chi^*_{n'l'm}(\mathbf{r}_a;\zeta_a)\, \chi_{nlm}(\mathbf{r}_b;\zeta_b) &= \hat{\mathcal{Z}}_{lm}(\nabla_a) \left(-\frac{\partial}{\partial\zeta_a}\right)^{n'-l'} \left(-\frac{1}{\zeta_a}\frac{\partial}{\partial\zeta_a}\right)^{l'} \\ \times\, \hat{\mathcal{Z}}_{lm}(\nabla_b) \left(-\frac{\partial}{\partial\zeta_b}\right)^{n-l} &\left(-\frac{1}{\zeta_b}\frac{\partial}{\partial\zeta_b}\right)^{l} \int d\mathbf{r}\, \frac{e^{-\zeta_a r_a}}{r_a}\, \frac{e^{-\zeta_b r_b}}{r_b}.\end{aligned} \tag{2.5.4}$$

The remaining integral can be worked out with elementary methods and reads

$$\int d\mathbf{r}\, \frac{e^{-\zeta_a r_a}}{r_a}\, \frac{e^{-\zeta_b r_b}}{r_b} = \frac{4\pi}{R}\frac{1}{\zeta_a^2-\zeta_b^2}\left(e^{-\zeta_b R} - e^{-\zeta_a R}\right). \tag{2.5.5}$$

In essence, the shift method has allowed to trade a difficult integration in the original problem for a difficult differentiation. Since it is often considered that differentiation is a fundamentally simpler task than the integration, this appears to be a considerable progress. However, the actual situation is slightly more complicated. First, the differentiations typically produce rather lengthy expressions. This poses a serious

challenge both at the implementation stage and for the efficiency of the resulting computer program. Even in the simple case considered above the final formula is rather complicated (we do not present it here, but the full form can be found in Ref. [311]). This problem is magnified for two-electron matrix elements where four independent orbitals are present in the integrand. The second weakness of the shift method is the numerical stability. This is illustrated well even by our simple example. One can see that the last term in Eq. (2.5.5) involves a numerical cancellation for $\zeta_a \approx \zeta_b$. Moreover, there is an apparent singularity for $\zeta_a = \zeta_b$, so this case would require a separate treatment, increasing the complexity of the algorithm. The occurrence of such cancellations suggests that significant numerical problems would arise if the basic formula was differentiated a considerable number of times.

Nonetheless, the shift method is a promising tool for the evaluation of many matrix elements within the STOs basis set. It can be applied, in principle, to almost any integral, so it provides a serious alternative when other methods fail or become intractable. Since the pioneering paper of Fernández Rico and coworkers [302] the shift method has been applied to several standard one-electron integrals [227], multipole moments integrals [312], electrostatic potential integrals [313], two-electron Coulomb integrals [314], two-electron four-centre integrals [315] and some others (see Refs. [226, 316] for a comprehensive summary). Typically, the shift method has been combined with other schemes such as the Gauss transform [311] or the momentum space methods [317].

2.6. Master integral approach of Pachucki

In his 2009 paper Pachucki single-handedly introduced a completely new method for the calculation of the two-centre integrals with exponential functions [318]. This work drew inspiration from the previous papers of several authors [319–326] devoted to the three-electron atomic integrals where the momentum space representation was used. Pachucki realised that the simplest two-centre integral with inverse powers of all interparticle distances (the master integral)

$$f(r) = \int \frac{d^3r_1}{4\pi} \int \frac{d^3r_2}{4\pi} \frac{e^{-u_3\, r_{1A}}}{r_{1A}} \frac{e^{-u_2\, r_{1B}}}{r_{1B}} \frac{e^{-w_2\, r_{2A}}}{r_{2A}} \frac{e^{-w_3\, r_{2B}}}{r_{2B}} \frac{r}{r_{12}}, \tag{2.6.1}$$

where r is the internuclear distance, can be obtained as a Laplace transform of some basic atomic integral. This fact was first pointed out by Fromm and Hill [319], but

has never been used in practice before. With the help of the so-called integration-by-parts identities, which are routinely used in evaluation of the Feymann diagrams [327, 328], Pachucki managed to derive the following differential equation for $f(r)$

$$rf''(r) + f'(r) - p^2 rf(r) + F(r) = 0, \tag{2.6.2}$$

where p^2 is a rational function in all nonlinear parameters and $F(r)$ is a complicated function involving exponential integrals and some elementary functions. The solution of this differential equation can be found with standard techniques, giving

$$f(r) = I_0(pr) \int_r^\infty dr'\, F(r') K_0(pr) + K_0(pr) \int_0^r F(r')\, I_0(pr), \tag{2.6.3}$$

where I_0 and K_0 are the modified Bessel functions. Therefore, the six-dimensional integral (2.6.1) has been reduced to a sum of one-dimensional integrations. The latter integral probably cannot be evaluated in a closed-form, but nonetheless is very straightforward to obtain numerically. To increase the powers of the interparticle distances under the integral sign in Eq. (2.6.1) Pachucki devised a series of recursion relations. They are very complicated and operate in six dimensions, but include no infinite summations and are given in a closed-form. Therefore, only the master integral needs to be evaluated numerically. This method was applied to the calculation of the Born-Oppenheimer potential for the ground state of the hydrogen molecule [329] and helium hydride [330], and several excited states of H_2 [331–334]. Later, extensions of the theory to the integrals involving Slater geminals ($e^{-\gamma r_{12}}$) were presented [335, 336].

Despite the apparent simplicity of the master integral method, it is marred by considerable difficulties. The first problem is that the recursive formulae [and the function $F(r)$ itself] possess numerous singularities, e.g. when some of the nonlinear parameters coincide. In order to develop a general method all these singularities need to be removed. Our experience shows that this leads to a huge number of special cases which have to be implemented separately. This is probably the reason why Pachucki abandoned direct applications of his method and reverted to the power series expansions in r of all integrals. The second problem is the numerical stability. Recursive relations which increase the powers of interelectronic distances are inherently numerically unstable. To give reliable results they need to be carried out in an extended precision, involving many tenths of significant digits. For a few-body system this is not a problem since multiprecision is typically required anyway and in-

tegrals can be evaluated once and stored. Moreover, basis sets for few-body systems typically involve only a few length scales and the nonlinear parameters are restricted to some special combinations (e.g. the James-Coolidge basis [2]). For many-electron systems this is no longer the case. Large basis sets for many-electron atoms involve many tens of length scales, so that arbitrary combinations of the nonlinear parameters appear in the integrals. Moreover, extended arithmetic precision cannot be used freely as the computational overhead is simply too large.

2.7. *B*-FUNCTIONS AND MOMENTUM SPACE TECHNIQUES

B-functions [337, 338, 306, 339] constitute a special class of exponential-type orbitals. Many authors consider them to be a legitimate basis set on their own, without any reference to Slater-type orbitals or others [340]. In the coordinate space the unnormalised *B*-functions were defined by Filter and Steinborn [337] as follows

$$B^m_{nl}(\alpha, \mathbf{r}) = \frac{\hat{k}_{n-1/2}(\alpha r)\, Y_{lm}(\alpha \mathbf{r})}{2^{n+l}\,(n+l)!}, \tag{2.7.1}$$

where the radial part is the so-called reduced Bessel function, $\hat{k}_\nu(z) = \sqrt{\frac{2}{\pi}} z^\nu K_\nu(z)$, and K_ν are the modified Bessel functions. Note that the factor of $\hat{k}_\nu(z)$ can be rewritten as a simple polynomial in z times the exponential, e^{-z}. This suggests that *B*-functions are indeed closely related to the conventional Slater-type orbitals. In the simplest case $n = l + 1$ (canonical STOs) we have

$$\chi_{l+1,lm}(\mathbf{r}) = B^m_{1,l}(\alpha, \mathbf{r}). \tag{2.7.2}$$

For larger n the corresponding transformation formula is considerably more involved. Nonetheless, *B*-functions can be written as a (finite) linear combination of STOs with higher principal quantum number (and *vice versa*) [126, 127, 341]. The same is true for other exponential-type functions such as the hydrogenic orbitals [181, 342].

The main reason for considering the *B*-functions in actual applications is their exceptionally simple momentum space representation (i.e. the Fourier transform). The following result was first derived by Weniger [306, 339] and independently by

Niukkanen [343]

$$\int \frac{d\mathbf{r}}{(2\pi)^{3/2}} B_{nl}^{m}(\alpha,\mathbf{r})\, e^{-i\mathbf{p}\cdot\mathbf{r}} = \sqrt{\frac{2}{\pi}}\, \frac{\alpha^{2n+l-1}}{(\alpha^2+p^2)^{n+l+1}}\, Y_{lm}(-i\mathbf{p}). \tag{2.7.3}$$

It must be noted that the corresponding formula for STOs is much more complicated and involves cumbersome summations over a range of quantum numbers plus some special functions [344–346]. Interestingly, the B-functions possess also a simple Gaussian integral representation. As shown by Shavitt [213]

$$\hat{k}_{\nu}(z) = \sqrt{\frac{2}{\pi}} \int_0^{\infty} dt\, \frac{e^{-zt^2-1/4t}}{(2t)^{\nu+1}}. \tag{2.7.4}$$

The above functions were used in the electronic structure calculations as early as in 1970 [347–349]. Note that a simple formula for the overlap integrals of the B-functions exists. Quite amazingly, an integral of the product of two B-functions with the same exponents is a linear combination of B-functions with different arguments [338]. This property was used numerous times in derivations of one-range addition theorems for B-functions [126–130].

Let us now turn our attention to the evaluation of the matrix elements involving B-functions. Because of the aforementioned favourable properties, the most widely used techniques were based on the momentum space representations. This led to numerous papers dealing with the overlap integrals [350–355], nuclear attraction integrals [356–360], and Coulomb integrals over the B-functions [361–366]. Other types of matrix elements were also considered, but these applications are less frequent [367–374]. Generally speaking, application of the Fourier transform techniques allows for significant simplifications of many important integrals. By transforming matrix elements to the momentum space the angular integrations can be carried out relatively easily, leaving only some radial integrals. The precise form of these integrals depends on a particular problem, but in the simplest case one has

$$\int_0^{\infty} dp\, \frac{p^{2k+l}\, j_l(pR)}{(\alpha^2+p^2)^m\, (\beta^2+p^2)^n}, \tag{2.7.5}$$

where k, l, m, n are all non-negative integers, and α, β are positive real numbers. This is the most troublesome aspect of the Fourier transform techniques and several novel methods of handling these integrals were proposed. For example, partial fraction decomposition can be applied to combine two factors in the denominator into a single

one. Unfortunately, this method leads to a drastic digital erosion, especially when the parameters α and β differ significantly. Another technique is based on various infinite series expansions. The drawback is that they are difficult to control and converge poorly for some combinations of the parameter values. Finally, numerical integration of the above integrals is conceivable. Sadly, the spherical Bessel functions j_l present in the integrand are highly oscillatory, especially for large R. This poses a serious challenge for the standard Gaussian quadratures - the results converge slowly with increasing number of the integration nodes. To overcome this problem a number of methods were proposed. This includes Möbius-type quadratures [352, 357, 375] and several acceleration techniques [356, 367, 376]. The most successful schemes are probably the so-called D and $\bar{D}$ nonlinear sequence transformations developed by Sidi and collaborators [360, 366, 370, 372, 374, 377–380]. Later, the same authors introduced a modified SD sequence transformation with somewhat better characteristics [381–383]. This field of research is still very active with many relevant papers published in recent years [199, 384–391]. The same can be said about applications of the Fourier transform techniques to calculation of various matrix elements and other improvements [189, 317, 393–402].

2.8. Miscellaneous methods

In this section we discuss a few methods for the evaluation of the STOs matrix elements which do not fall in any category described above. Some of them are relatively new and promising developments but are not fully explored yet. Because of that we discuss them only superficially, but attempt to provide reasonable literature and signal their importance.

The first method is the so-called Coulomb resolution introduced by Varganov et al. in 2008 [403] and elaborated in a subsequent series of papers [404–410]. The main idea is to represent the Coulomb interaction as a sum over some auxiliary functions, i.e. $r_{12}^{-1} = |\phi_i\rangle\langle\phi_i|$. While this idea is not entirely new, the truly novel aspect of the method is how the functions ϕ_i are constructed. It was shown that a convenient starting point is a set of functions f_i which are orthonormal with respect to the weight r_{12}^{-1}, i.e. $\langle f_i|r_{12}^{-1}|f_j\rangle = \delta_{ij}$. The authors of Ref. [403] proved that this condition is satisfied when the radial part of f_i is chosen as $\int_0^\infty dx\, x^2 j_l(xr)\, h_n(r)$, where j_l are the spherical Bessel functions and h_n form an orthonormal and complete set on $[0, \infty)$ but are otherwise arbitrary. The spherical part of f_i is composed of the

usual spherical harmonics. Under these conditions the potential functions take the following simple form: $\phi_i = 2\sqrt{2}\,Y_{lm}(\theta,\phi)V_{nl}(r)$, where $V_{nl}(r) = \int_0^\infty dx\, j_l(xr)\, h_n(r)$. Originally, the Coulomb resolution technique was not introduced in the context of STOs. However, it was quickly realised by Hoggan [411, 412] that such application is indeed possible. In two recent papers he has shown that the Coulomb resolution can be applied to get rid of three- and four-centre integrals over STOs. The biggest advantage of this approach is comparatively low computational cost. Unfortunately, it is not known how accurate the Coulomb resolution is for higher angular momentum functions and how many terms are necessary to achieve convergence in this case.

Another important and active field of study is the use of non-integer STOs as a basis set in calculations for atoms and molecules (i.e. STOs with non-integer principal quantum number, n). There are many valid reasons for introducing such a basis set, from remarkable improvements in flexibility of the trial wavefunctions [413–417] to considerable advantages in solving the four-component Dirac equation due to the so-called kinetic balance condition [418–420]. Historically, the first attempts to evaluate the integrals involving non-integer STOs were made by Silverstone [421, 422], Geller [423, 424], and Bishop and Leclerc [425]. These authors utilised the Fourier transform of the non-integer STOs to find analytic expressions for the necessary matrix elements and thus suffered from the usual problems of the momentum space methods (*vide supra*). Nonetheless, further improvements of the Silverstone scheme were published [237, 393, 394]. Other techniques proposed in the literature since then have employed the ellipsoidal coordinates [426–430] or single-centre methods [138, 431–440]. Unfortunately, both techniques contain infinite series in the final expressions and recent works suggest that they are pathologically slowly convergent [441] or even divergent [442, 149] in general case. This made several authors resort to purely numerical methods [441, 443–447]. While it seems that the perspective of molecular calculations with non-integer STOs is still remote, many interesting results have been generated for atoms in recent years (see, for example, Refs. [448–451] and references therein).

Symbolic computation methods [452] are the offspring of relatively recent developments in the scientific software. The main idea is rather natural for the human beings. Instead of performing calculations with the floating-point numbers, let the computer operate on symbolic expressions. There are many advantages of such approach. First, the computers can derive and manipulate analytic expressions beyond capabilities of individual humans. Second, the final expressions need to be derived

only once and then can be stored for further use, eliminating the expensive recalculations when the parameters change. Finally, symbolic calculations are free of any numerical instabilities since all numbers are represented either by abstract symbols or by integers (and ratios thereof). In the context of STOs, the third property is of uttermost importance. This approach to calculation of STOs matrix elements was pioneered by Jones and co-workers (see Refs. [161–164] and the other papers of the same authors). A similar approach was pursued by Righi and Kuhnen [453], Safouhi et al. [360, 454], and Harris [273]. Recently, Barnett has published a series of papers where the power of symbolic computation was illustrated by generating analytic expressions for overlap, Coulomb and other integrals over STOs [455–459]. Unfortunately, these symbolic calculations are orders of magnitude slower than the corresponding floating-point evaluations. Therefore, the method of Barnett seems to be limited (for the time being) to generating reference values to calibrate and test the conventional programs. This may change in the future with improvements in symbolic software packages such as MATHEMATICA [460] or MAPLE [461].

CHAPTER 3

Main results of the thesis

Paper I

"Reexamination of the calculation of two-center, two-electron integrals over Slater-type orbitals. I. Coulomb and hybrid integrals"

Michał Lesiuk and Robert Moszyński

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Commentary

This paper constitutes the first paper of the series and is devoted to detailed study of the Coulomb and hybrid integrals over STOs for the diatomic molecules. The main goal is to develop analytic and/or semi-analytic techniques for the‘ calculation of these integrals satisfying several important requirements. First, the method must be general with respect to the quantum numbers of the orbitals and their screening constants. This property is indispensable in spectroscopically accurate calculations for diatomics where large one-electron basis sets must be used to reach saturation of the results. Second, the method must possess a decent computational efficiency allowing to calculate the integrals in (at most) several microseconds per integral seed. Third, the new techniques must be sufficiently numerically stable so that the digital erosion can be tightly controlled maintaining (at least) $10 - 12$ significant digits in the final result without resorting to arbitrary-precision arithmetic systems.

At the initial stage of the study we tested several methods for the calculation of the Coulomb and hybrid matrix elements which are available in the literature. Unfortunately, we found that all of them are somewhat lacking in the present context. For example, some schemes perform well for low quantum numbers but become

very complicated (and numerically inefficient) in the general case. Others contain significant numerical cancellations and give inaccurate results for some combinations of the exponents. This prompted development of a new method, free of the aforementioned problems.

Our scheme for the calculation of the Coulomb and hybrid integrals is comprised of two fairly independent schemes which have a complementary numerical stability. Both methods start with the analytic integration over the coordinates of one of the electrons, but differ in how the remaining integrations are carried out. In the first scheme all quantities are expressed in terms of the ellipsoidal coordinates. While this idea is not new, we proposed a novel semi-numerical scheme where the last (one-dimensional) integration is carried out numerically. We argue that this allows to remove almost all numerical problems found in the previous approaches. Moreover, the last numerical integration is a relatively simple step because the integrand is a smooth and well-behaved function and can be calculated recursively with an optimal speed and precision. Note that this situation is rather unusual - having analytic expressions for the result of the integration one still prefers to perform it numerically.

The second component of the new method is a recursive scheme utilising relations between the Legendre polynomials of different order (and several other simple relations) to reduce all integrals to basic quantities involving only ns orbitals. The latter are solved in terms of the confluent hypergeometric function which can be evaluated very efficiently in the present case.

Finally, we present numerical results proving that by combining the two schemes described above one is able to calculate the Coulomb and hybrid integrals with sufficient precision up to $l = 6$ and within the $2^{-4} - 2^{8}$ range of the screening constants. Crucially, it is sufficient to use only the double or quadruple arithmetic precision to achieve this goal. Let us also note that since the publication of Paper I we have found further improvements in the ellipsoidal method. They are related primarily to the transformation between the ellipsoidal and spherical coordinate systems and are detailed in the *Unpublished results* section of the thesis.

Reexamination of the calculation of two-center, two-electron integrals over Slater-type orbitals. I. Coulomb and hybrid integrals

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In this paper, which constitutes the first part of the series, we consider calculation of two-center Coulomb and hybrid integrals over Slater-type orbitals. General formulas for these integrals are derived with no restrictions on the values of the quantum numbers and nonlinear parameters. Direct integration over the coordinates of one of the electrons leaves us with the set of overlaplike integrals which are evaluated by using two distinct methods. The first one is based on the transformation to the ellipsoidal coordinates system and the second utilizes a recursive scheme for consecutive increase of the angular momenta in the integrand. In both methods simple one-dimensional numerical integrations are used in order to avoid severe digital erosion connected with the straightforward use of the alternative analytical formulas. It is discussed that the numerical integration does not introduce a large computational overhead since the integrands are well-behaved functions, calculated recursively with decent speed. Special attention is paid to the numerical stability of the algorithms. Applicability of the resulting scheme over a large range of the nonlinear parameters is tested on examples of the most difficult integrals appearing in the actual calculations including, at most, $7i$-type functions ($l = 6$).

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I. INTRODUCTION

Slater-type orbitals [1,2], or more general exponential-type orbitals, are the natural choice of basis set for applications in quantum chemistry and molecular or atomic physics. Their common origin is the analytical solution of the Schrödinger equation for the hydrogen atom. It can be shown that Slater-type orbitals behave correctly at the electron-nucleus coalescence points; i.e., they satisfy Kato's conditions [3]. Additionally, the Slater-type orbitals decay exponentially when an electron is far from the nucleus. This is in line with the theoretical findings of the asymptotic form of the electron density [4]. It is obvious that Gaussian orbitals [5], which have gained enormous popularity in the past 50 years, are able to satisfy neither of the above conditions. Virtually the only issue which prohibited the widespread use of the Slater-type orbitals is the calculation of the two-electron molecular integrals.

The main purpose of the present series of papers is to provide a complete set of methods for the evaluation of the two-electron, two-center integrals. The reliability of these methods needs to be sufficient to allow the use of Slater-type orbitals including high angular momentum functions for the diatomic systems. Our integral program based on the presented algorithms serves as a vehicle for the upcoming new *ab initio* quantum chemistry program package KOŁOS. This program combines a basis set of Slater-type orbitals with state-of-the-art quantum chemical *ab initio* methods and is aimed at spectroscopically accurate (few cm^{-1}) results for the diatomic systems.

When considering our approach to the present problem, one issue needs to be clarified. To reach the spectroscopic accuracy it is not only necessary to use huge basis sets but also very accurate quantum chemistry methods. Let us now observe that calculations of the two-electron integral file scale as the fourth power of the size of the system (N^4) in the worst-case scenario. This can be compared with the scaling of the accurate coupled-cluster methods, N^6 for CCSD, N^8 for CCSDT, etc., [6–9]. As a result, one can expect that calculations of the integral file should not be a bottleneck in high-level calculations of the correlation energy. On the other hand, since we require the aforementioned accuracy in the molecular energy, we need the integrals to be calculated with higher precision than typical. We believe that the requirement for accuracy of 12 decimal places is reasonable.

The situation described above suggests that we should favor accuracy of the algorithms over their speed. In other words, if we had two algorithms—the first one being fast but less accurate and the second one being somehow slower but significantly more accurate—we would pick up the second one. Of course, we still have limitations on the computational time and we cannot use arbitrary precision arithmetic, for instance. This philosophy of choosing and developing algorithms is perceptible throughout the whole series of papers.

This series of papers is organized as follows. In Paper I we deal with calculation of the Coulomb and hybrid integrals, i.e., $(aa|bb)$ and $(aa|ab)$, respectively, where a and b denote the nuclei at which orbitals are located. We use direct integration over the second electron in the same spirit as several previous investigators but we differ in methods of computation of almost all nontrivial basic quantities. Final forms of the working expressions are also completely reformulated. Moreover, we present the results of demanding tests of the numerical performance. In Paper II we apply the Neumann expansion to calculation of the exchange integrals, $(ab|ab)$. We report new methods of calculation of the most difficult auxiliary quantities appearing in the theory. Additionally, we discuss how new algorithms can be sewed together to form a sufficiently general method. Finally, in Paper III we provide the first application of the presented theory, *ab initio* calculations for the beryllium dimer which is an interesting system from both spectroscopic and theoretical points of view. In these calculations we use Slater-type orbital (STO) basis sets ranging from double to sextuple ζ quality combined with high-level

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ab initio methods in order to provide spectroscopically accurate results.

The literature dealing with evaluation of the molecular integrals over STOs is extensive and a full bibliography would count hundreds of positions. Its detailed review is undoubtedly beyond the scope of the present report. Therefore, our introduction is, by necessity, limited and subjective. Nonetheless, let us recall several prominent and the most widely used general techniques for computation of the aforementioned integrals.

Single-center expansions make it possible to expand STOs located at some point of space around a different center. These methods were pioneered by Barnett and Coulson as the widely known ζ-function method [10–12] and later independently by Löwdin [13] (α-function method). In cases when the single-center expansion terminates under the integral sign due to spherical symmetry of the integrand, it typically results in closed-form, compact, and plausible expressions. However, in many cases, such as calculation of the exchange integrals, the single-center expansions result in an infinite series which have a pathologically slow (i.e., logarithmic) convergence rate [14]. The problem does not have a satisfactory solution, although several approaches [15] were adopted to overcome it. The second problem of the single-center expansions is the catastrophic digital erosion during calculations of the auxiliary quantities [16,17], which seems to be extremely difficult to overcome. A promising work-around is the use of the symbolic computational environments such as *Mathematica* [18–20], but at present the symbolic methods are typically orders of magnitude slower than the numerical ones. Since the time the single-center methods were first proposed, several new (or more general) expansion techniques have been developed. Examples are the works of Guseinov [21], Harris and Michels [22], and Rico *et al.* [23,24] and references therein.

The second class of methods which gained a significant interest is the Gaussian expansion methods and the Gaussian transform methods. The former is simply based on a least-squares fit of a linear combination of Gaussian orbitals in order to mimic the shape of STOs. This idea, proposed first by Boys and Shavitt [25], was the dominant method used in the early versions of the SMILES program [26]. The Gauss transform methods are more involved and use some integral representations in order to transform STO into a more computationally convenient form. The initial proposition of Shavitt and Karplus [27–29] was to use the Laplace transform of the exponential function but now a handful of different schemes is in use, along with suitable discretization techniques [30].

The next prominent technique is the family of Fourier-transform methods which are usually used in conjunction with the so-called B functions. These methods were primarily developed by the group of Steinborn [31–41] and applied to many difficult cases of the many-center integrals. The fact that B functions, being essentially a linear combination of STOs, possess an exceptionally simple Fourier transform can be used to evaluate the integrals in the momentum space and reduce many important integrals to the combination of some one-dimensional integrals. However, these integrals contain highly oscillatory integrands (including the Bessel functions), which make numerical integration extremely difficult with standard Gaussian quadrature techniques. Some approaches were adopted to accelerate the convergence towards the exact value with increasing number of quadrature nodes. The prominent method is the SD transform, put forward by Sidi [42,43] and later applied by Safouhi *et al.* [44,45]. Despite that, it seems that there is no general method reliable enough to evaluate the integrals in question in a black-box fashion.

There is also a number of less extensively studied techniques for evaluation of the molecular integrals over STOs. These include the Coulomb Sturmians introduced by Shull and Löwdin [46] and used by some other authors [47–50]. The shift operator technique [51–53] is a very elegant method which generates integrals with arbitrary STOs starting with the simplest integrals with $1s$ functions by application of the so-called shift operator. Gill *et al.* [54,55] introduced the Coulomb resolution techniques where the interaction potential is expanded in terms of the so-called potential functions resulting from the the Poisson equation. This method has been recently pursued by Hoggan and co-workers [56,57] and included in their STOP program package [58].

Remarkably, it has not been a well-known fact yet that all two-center integrals over STOs were integrated analytically in a closed form. In a recent work, Pachucki [59,60] has shown that the so-called master integral with inverse powers of all interparticle distances can be obtained from the second-order differential equation in the distance between the nuclei. The present authors also contributed to the development of this theory by extending it to the case of Slater geminals [61]. Pachucki used these expressions for calculations of the Born-Oppenheimer potential for the hydrogen molecule [62,63] and helium hydride ion [64]. However, an extreme level of complication of this theory along with drastic numerical instabilities occurring in the calculations have made its use limited to certain special forms of the basis set, applicable only to two-electron systems. We believe that some ingenious reformulation of this theory is necessary to circumvent the aforementioned difficulties.

We postpone the discussion of the methods based on the Neumann expansion of the interaction potential in the ellipsoidal coordinates. In the second paper of the series it is used to evaluate the exchange integrals and a proper separate introduction is given therein.

Let us now concentrate on methods designed specifically for treatment of the Coulomb and hybrid integrals. For the former ones there exists a plethora of independent methods which differ in both accuracy and speed. Probably the first attack on this problem was attempted by Barnett and Coulson [10] by using the single-center expansion technique. Roothaan [65] pioneered the direct integration method in the ellipsoidal coordinates which was later pursued by several authors [66–72]. Later, it became apparent that integration in the momentum space utilizing the Fourier representation of STOs is very advantageous [34,35,73–77]. Gaussian transform techniques [27,28,78], refined translation or expansion methods [79–81], and several special approaches [78,82–87] were also successfully applied. For hybrid integrals the number of available methods is modest. Several prominent techniques, such as the Fourier transform, cannot be applied straightforwardly. The biggest effort was aimed at the direct

integration [66,88–90] or its combinations with the translation techniques [91–93]. Our unified approach to the Coulomb and hybrid integrals is based on the earlier experiences with the direct integration. By using the Laplace expansion of the interaction potential and analytic integration over the coordinates of the second electron the problem is reduced to the calculation of the standard overlap integrals and a set of *overlaplike* integrals. To calculate these integrals, two distinct approaches are used. The first one is integration in the ellipsoidal coordinates and the second method is based on recursive techniques. In both cases a simple, one-dimensional numerical integration is used to avoid drastic digital erosion. This indicates some connections with the method of Miller [90]. Finally, we verify that when both methods are used together, in their respective regions of applicability, a loss of digits observed in the calculations by using some other methods can be avoided within a reasonable range of the nonlinear parameters.

Let us also note in passing that to perform actual calculations on the diatomic systems one also requires one-electron, two-center and two-electron, one-center (atomic) integrals. The former can be computed using various techniques, among which the Fourier transform methods [31–41], recursive techniques for increasing the angular momenta in the integral [78,94–99], and finally direct integration using the ellipsoidal coordinate system [65,100–102] were intensively studied. The latter seems to be the method of choice for these integrals. Two-electron atomic integrals have been solved at least since the papers of Clementi and co-workers (see Refs. [103] and references therein). For the sake of completeness, a refined, simple, and numerically stable procedure for the computation of these integrals was included in the Supplemental Material [104].

II. PRELIMINARIES

Let us consider a diatomic system with the nuclei A and B centered at the positions $\mathbf{R}_A = (0,0,-R/2)$ and $\mathbf{R}_B = (0,0,R/2)$, respectively, in the ordinary Cartesian coordinate system. Slater-type orbitals have the following general form:

$$\chi_{nlm}(\mathbf{r};\zeta) = S_n(\zeta) r^{n-1} e^{-\zeta r} Y_{lm}(\theta,\phi). \tag{1}$$

Therefore, any STO is uniquely described by the quartet of parameters (n,l,m,ζ). We assume throughout that n, l are restricted to the positive integers ($n > l$). The variables r_a, θ_a, ϕ denote the spherical coordinates located on the atom A with analogous notation for the center B. In Eq. (1), $S_n(\zeta)$ is the radial normalization constant,

$$S_n(\zeta) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}}, \tag{2}$$

and $Y_{lm}(\theta,\phi)$ are the spherical harmonics defined according to the Condon-Shortley phase convention [105],

$$Y_{lm}(\hat{\mathbf{r}}) = \Omega_{lm} P_l^{|m|}(\cos\theta) \frac{e^{im\phi}}{\sqrt{2\pi}}, \tag{3}$$

where P_l^m are the (un-normalized) associated Legendre polynomials [106] and Ω_{lm} is the angular normalization constant:

$$\Omega_{lm} = i^{m-|m|} \sqrt{\frac{2l+1}{2} \frac{(l-|m|)!}{(l+|m|)!}}. \tag{4}$$

In actual calculations it is typical to use real versions of the spherical harmonics. However, the complex spherical harmonics are more convenient in the derivations and thus we use them throughout the paper. Transfer to the real spherical harmonics can be performed on the top of the presented algorithms by using standard relations.

Let us now introduce the prolate ellipsoidal coordinates (ξ,η,ϕ) by means of the relations,

$$\xi = \frac{r_a + r_b}{R}, \quad \eta = \frac{r_a - r_b}{R}, \tag{5}$$

so that $1 \leqslant \xi \leqslant \infty$, $-1 \leqslant \eta \leqslant 1$, and $0 \leqslant \phi \leqslant 2\pi$. The spherical coordinates are expressed through the ellipsoidal coordinates by means of the well-known expressions

$$r = \frac{R}{2}(\xi + \kappa\eta), \quad \cos\theta = \frac{1+\kappa\xi\eta}{\xi+\kappa\eta}, \tag{6}$$

where the value of κ is equal to $+1$ if STO is located on the center A or -1 if it is located on the center B. The volume element becomes $d\mathbf{r} = (\frac{R}{2})^3(\xi^2-\eta^2)\,d\xi\,d\eta\,d\phi$. The simplest way to express the product of two STOs (i.e., the charge distribution) in the ellipsoidal coordinates is to proceed in two steps. First, we transfer the following scaled product of the Legendre polynomials by means of the expression

$$P_{l_a}^{|m_a|}(\cos\theta_a) P_{l_b}^{|m_b|}(\cos\theta_b) r_a^{l_a} r_b^{l_b} = \left(\frac{R}{2}\right)^{l_a+l_b} [(\xi^2-1)(1-\eta^2)]^{|M|/2} \sum_{p=0}^{\Gamma} \sum_{q=0}^{\Gamma} \left(\Xi_{l_a l_b}^M\right)_{pq} \xi^p \eta^q, \tag{7}$$

where $M = m_a - m_b$, $\Gamma = l_a + l_b$, and $\Xi_{l_a l_b}^M$ are square matrices of dimension Γ. The values of the latter depend on the locations of the orbitals and their quantum numbers. Explicit forms of these matrices can easily be deduced from the general expressions available in the literature [107–111]. We tabulated the values of $\Xi_{l_a l_b}^M$ up to the maximum value of $l_a + l_b$ equal to 24. These tables, along with *Mathematica* code [112] used for their generation, can be obtained from the authors on demand.

The remainder can be transferred to the ellipsoidal coordinates by using the formula

$$r_a^{n_a} r_b^{n_b} = \sum_{k=0}^{k_{\max}} B_k^{n_a n_b} \xi^k \eta^{k_{\max}-k}, \tag{8}$$

with $k_{\max} = n_a + n_b$. The above expression has been extensively used by many authors [110,113,114] who presented explicit expressions for the coefficients $B_k^{n_a n_b}$ (the so-called generalized binomial coefficients). We found it simpler to tabulate these coefficients as series of one-dimensional lookup tables.

Making use of the transfer relations (7) and (8) one can write down the explicit expression for the STOs charge distribution in terms of the ellipsoidal coordinates. The result reads (for

convenience, we additionally included the Jacobian)

$$\left(\frac{R}{2}\right)^3 (\xi^2-\eta^2)\chi^*_{n_a l_a m_a}(\mathbf{r}_a;\zeta_a)\chi_{n_b l_b m_b}(\mathbf{r}_b;\zeta_b) = \frac{K_{ab}}{2\pi} e^{-\alpha\xi-\beta\eta}[(\xi^2-1)(1-\eta^2)]^{|M|/2} e^{iM\phi} \times \sum_{k=0}^{k_{\max}} B_k^{n_a-l_a,n_b-l_b} \sum_{p=0}^{\Gamma}\sum_{q=0}^{\Gamma} \left(\Xi^M_{l_a l_b}\right)_{pq} \xi^{p+k}\ \eta^{q+k_{\max}-k}, \tag{9}$$

with $M = m_a - m_b$, $k_{\max} = n_a - l_a + n_b - l_b$, and $\Gamma = l_a + l_b$. Additionally, in Eq. (9) we introduced several new quantities: $\alpha = \frac{R}{2}(\zeta_a+\zeta_b)$, $\beta = \frac{R}{2}(\kappa_a\zeta_a+\kappa_b\zeta_b)$, $K_{ab} = S_{n_a}(\zeta_a)S_{n_b}(\zeta_b)\,\Omega_{l_a m_a}\Omega_{l_b m_b}(\frac{R}{2})^{n_a+n_b+1}$. The above formulation is quite explicit and rather transparent at the same time. Apart from that, it remains valid for "singular" orbitals such as $0s$, which is advantageous from the point of view of some developments.

Before passing further, let us introduce three useful auxiliary functions:

$$A_p(\alpha) = \int_1^\infty d\xi\ \xi^p e^{-\alpha\xi}, \tag{10}$$

$$B_q(\beta) = \int_{-1}^{+1} d\eta\ \eta^q e^{-\beta\eta}, \tag{11}$$

$$a_p(\alpha) = \int_0^1 d\xi\ \xi^p e^{-\alpha\xi}. \tag{12}$$

The first two of the above functions are the so-called Mulliken integrals [100]. Accurate and stable calculation of these integrals was considered by many authors; the works of Corbató [101] and a recent paper of Harris [115] need to be mentioned in this respect. The third integral, Eq. (12), can be considered complementary to the first integral, Eq. (10), and has strong connections with the lower incomplete γ functions. Integrals (12) have to be computed by using the Miller algorithm [116], as discussed by Harris [117].

III. COULOMB AND HYBRID INTEGRALS

In this section we attack the main objectives of this paper: calculation of the Coulomb (I_C) and hybrid (I_H) integrals. With the notation developed in the previous section they take the following form:

$$I_C = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \chi^*_{n_1 l_1 m_1}(\mathbf{r}_{1a};\zeta_1)\chi_{n_2 l_2 m_2}(\mathbf{r}_{1a};\zeta_2) \times \frac{1}{r_{12}}\, \chi^*_{n_3 l_3 m_3}(\mathbf{r}_{2b};\zeta_3)\chi_{n_4 l_4 m_4}(\mathbf{r}_{2b};\zeta_4), \tag{13}$$

$$I_H = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \chi^*_{n_1 l_1 m_1}(\mathbf{r}_{1a};\zeta_1)\chi_{n_2 l_2 m_2}(\mathbf{r}_{1b};\zeta_2) \times \frac{1}{r_{12}}\, \chi^*_{n_3 l_3 m_3}(\mathbf{r}_{2b};\zeta_3)\chi_{n_4 l_4 m_4}(\mathbf{r}_{2b};\zeta_4). \tag{14}$$

Let us note that in the above expressions we have adapted a particular, fixed location of the STOs. This convention is very useful from the point of view of the upcoming derivation. Other possible options for the orbitals' location within the class of the Coulomb and hybrid integrals can be obtained by using the usual eightfold permutational symmetry of the integrals.

A. Initial reduction to the overlaplike integrals

Before proceeding with the integration of I_C and I_H, let us simplify the formulas by using the Clebsh-Gordan expansion of the products of the spherical harmonics. In the case of the Coulomb integrals one expands pairs of the spherical harmonics on both centers; in case of the hybrid integrals, only the pair dependent on the coordinates of the second electron can be expanded. Once the Clebsh-Gordan expansion is used and the resulting integrals are written explicitly, it becomes obvious that the problem reduces now to the calculation of the following families of the integrals:

$$\widetilde{I}_C = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, r_{1a}^{n_{12}-2}\, Y^*_{L_1 M}(\cos\theta_{1a},\phi)\,\frac{1}{r_{12}} \times r_{2b}^{n_{34}-2}\, Y_{L_2 M}(\cos\theta_{2b},\phi)\, e^{-\zeta_{12}r_{1a}-\zeta_{34}r_{2b}}, \tag{15}$$

$$\widetilde{I}_H = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, r_{1a}^{n_1-1}\, Y^*_{l_1 m_1}(\cos\theta_{1a},\phi) e^{-\zeta_1 r_{1a}} \times r_{1b}^{n_2-1}\, Y_{l_2 m_2}(\cos\theta_{1b},\phi) e^{-\zeta_2 r_{1b}}\,\frac{1}{r_{12}} \times r_{2b}^{n_{34}-2}\, Y_{L_2 M}(\cos\theta_{2b},\phi)\, e^{-\zeta_{34}r_{2b}}, \tag{16}$$

where $n_{12} = n_1 + n_2$, $\zeta_{12} = \zeta_1 + \zeta_2$, etc., and r_{ij} denote the interparticle distances. It is evident that any Coulomb integral (I_C) can be written as a linear combination of the pertinent integrals $\widetilde{I}_C$ and the correspondence between I_H and $\widetilde{I}_H$ is analogous. For convenience, we have also skipped the normalization constants S_n since their multiplicative presence is obvious and does not change throughout the derivation. When considering the coefficients that relate $I_{C/H}$ and $\widetilde{I}_{C/H}$, there is an additional effort connected with calculation of the Wigner $3J$ symbols (or equivalently the Clebsh-Gordan coefficients). Computation of these quantities is not a trivial problem and has been considered many times in the literature; see Refs. [118–123] as representative examples.

The first step of the integration proceeds in the usual manner: One integrates over the coordinates of the second electron. This is a quite natural approach since both orbitals of the second electron lie on the same center (B, in our convention). The formula for the necessary integral exists in the literature and appears independently in many works. The simplest way to arrive at the final expression is to use the Laplace expansion of $1/r_{12}$ in spherical coordinates relative to center B. Independently of the derivation route, one arrives at

$$\int d\mathbf{r}_2\, \frac{1}{r_{12}} r_{2b}^{n_{34}-2}\, Y_{L_2 M}(\cos\theta_{2b},\phi)\, e^{-\zeta_{34}r_{2b}} = \frac{4\pi}{2L_2+1}\,\frac{Y_{L_2 M}(\cos\theta_{1b},\phi)}{\zeta_{34}^{n_{34}}} \left[(\zeta_{34}r_{1b})^{n_{34}}\, a_{n_{34}+L_2}(\zeta_{34}r_{1b}) + (n_{34}-L_2-1)!\, e^{-\zeta_{34}r_{1b}} \sum_{j=L_2}^{n_{34}-1} \frac{(\zeta_{34}\,r_{1b})^j}{(j-L_2)!} \right], \tag{17}$$

where a_n is given by Eq. (12). To bring the above expression into a more familiar and simplified form, we could use the following obvious relationships:

$$a_n(\alpha) = \frac{n!}{\alpha^{n+1}} - A_n(\alpha), \tag{18}$$

$$A_n(\alpha) = \frac{e^{-\alpha}\, n!}{\alpha^{n+1}} \sum_{k=0}^{n} \frac{\alpha^k}{k!}. \tag{19}$$

By doing so, one expresses the integral (17) explicitly through the elementary functions only. It seems to be advantageous but there are two main problems connected with use of Eqs. (18) and (19). First, these expressions introduce spurious singularities (high inverse powers of r_{1b}) and generate integrals which have to be treated with special methods. Second, and more importantly, Eq. (18) by itself is numerically badly conditioned and these problems propagate to the final expressions for the Coulomb and hybrid integrals. Precisely speaking, unless the relationship $n \gg \alpha$ holds, Eq. (18) consists of subtraction of two large numbers to a relatively small result. Therefore, a huge digital erosion occurs, especially when large values of the quantum numbers are necessary.

This leads to the conclusion that in order to preserve a good numerical stability of the method, we have to abandon the use of Eqs. (18) and (19) and exploit Eq. (17) as it stands. By inserting Eq. (17) into the initial expressions for $\widetilde{I}_C$, one obtains the formula

$$\widetilde{I}_C = \frac{4\pi}{2L_2+1}\frac{1}{\zeta_{34}^{n_{34}}}\left[\zeta_{34}^{n_{34}} \int d\mathbf{r}_1\, r_{1a}^{n_{12}-2}\, Y_{L_1M}(\cos\theta_{1a},\phi)\, e^{-\zeta_{12}r_{1a}}\, r_{1b}^{n_{34}}\, Y_{L_2M}(\cos\theta_{1b},\phi)\, a_{n_{34}+L_2}(\zeta_{34}r_{1b}) \right.$$
$$\left. + (n_{34}-L_2-1)! \sum_{j=L_2}^{n_{34}-1} \frac{\zeta_{34}^{j}}{(j-L_2)!} \int d\mathbf{r}_1\, r_{1a}^{n_{12}-2}\, Y_{L_1M}(\cos\theta_{1a},\phi)\, e^{-\zeta_{12}r_{1a}}\, r_{1b}^{j}\, Y_{L_2M}(\cos\theta_{1b},\phi)\, e^{-\zeta_{34}r_{1b}} \right]. \tag{20}$$

For the hybrid integrals, the manipulations are slightly more involved. After inserting Eq. (17) into the formula for $\widetilde{I}_H$, one is left with three spherical harmonics under the integral sign. Two of these spherical harmonics are centered at nucleus B and therefore can be expanded in the Clebsh-Gordan series. The result of these manipulations is as follows (the usual notation for the Wigner $3J$ symbols is used):

$$\widetilde{I}_H = \frac{(-1)^{m_2}}{\zeta_{34}^{n_{34}}}\sqrt{(2l_2+1)(2L_2+1)} \sum_{L_1=|l_2-L_2|}^{l_2+L_2} \sqrt{\frac{4\pi}{2L_1+1}} \begin{pmatrix} l_2 & L_2 & L_1 \\ -m_2 & -M & m_1 \end{pmatrix} \begin{pmatrix} l_2 & L_2 & L_1 \\ 0 & 0 & 0 \end{pmatrix}$$
$$\times \left[\zeta_{34}^{n_{34}} \int d\mathbf{r}_1\, r_{1a}^{n_1-1}\, Y_{l_1m_1}(\cos\theta_{1a},\phi)\, e^{-\zeta_1 r_{1a}}\, r_{1b}^{n_2+n_{34}-1}\, Y_{L_1m_1}(\cos\theta_{1b},\phi)\, e^{-\zeta_2 r_{1b}}\, a_{n_{34}+L_2}(\zeta_{34}r_{1b}) \right.$$
$$\left. + (n_{34}-L_2-1)! \sum_{j=L_2}^{n_{34}-1} \frac{\zeta_{34}^{j}}{(j-L_2)!} \int d\mathbf{r}_1\, r_{1a}^{n_1-1}\, Y_{l_1m_1}(\cos\theta_{1a},\phi)\, e^{-\zeta_1 r_{1a}}\, r_{1b}^{n_2+j-1}\, Y_{L_1m_1}(\cos\theta_{1b},\phi)\, e^{-(\zeta_2+\zeta_{34})r_{1b}} \right]. \tag{21}$$

Let us now investigate the above formulas in a greater detail. It is obvious that Eqs. (20) and (21) include two basic types of integrals, which take the following general forms:

$$S_{n_1l_1m}^{n_2l_2m}(\zeta_1,\zeta_2) = \int d\mathbf{r}_1\, r_{1a}^{n_1-1}\, Y_{l_1m}(\cos\theta_{1a},\phi)\, e^{-\zeta_1 r_{1a}}\, r_{1b}^{n_2-1}\, Y_{l_2m}(\cos\theta_{1b},\phi)\, e^{-\zeta_2 r_{1b}}, \tag{22}$$

$$\widetilde{S}_{n_1l_1m}^{n_2l_2m}(n_3;\zeta_1,\zeta_2,\zeta_3) = \int d\mathbf{r}_1\, r_{1a}^{n_1-1}\, Y_{l_1m}(\cos\theta_{1a},\phi)\, e^{-\zeta_1 r_{1a}}\, r_{1b}^{n_2-1}\, Y_{l_2m}(\cos\theta_{1b},\phi)\, e^{-\zeta_2 r_{1b}}\, a_{n_3}(\zeta_3 r_{1b}). \tag{23}$$

The first integral is simply an overlap integral between two-center STO charge distributions, and for the second one let us introduce the name *overlaplike integral*. The latter differs from the former only by the presence of a_n function under the integral sign. Further, we concentrate solely on the overlaplike integrals and present two separate approaches. We verify that these two methods combined provide sufficient accuracy and reasonable speed to allow calculation of the desired Coulomb and hybrid integrals. We see no need to consider overlap integrals (22) separately. As one can see shortly, they can be computed by using exactly the same algorithms as integrals (23). The only differences lie in the fact that for the overlaplike integrals we use numerical integration to compute some of the basic quantities and for the overlap integrals, Eq. (22), this numerical integration can simply be skipped due to absence of the a_n factor.

B. Calculation of the overlaplike integrals by the ellipsoidal coordinates method

For the calculation of the overlaplike integrals the use of ellipsoidal coordinates seems to be a natural approach because

the standard one-electron integrals separate into a product of simple one-dimensional integrals. It is obvious, however, that, due to the presence of the factor a_n in Eq. (23), this separation can no longer be performed straightforwardly. Not discouraged by this fact, we proceed in a conventional manner and utilize Eq. (9) to express the integrand in Eq. (23) in elliptic coordinates. Noting that the axial symmetry of the integrand requires $M = 0$ in the transfer formula (9) we arrive at the expression

$$\begin{aligned}&\widetilde{S}^{n_2 l_2 m}_{n_1 l_1 m}(n_3;\zeta_1,\zeta_2,\zeta_3)\\ &\quad= K_{12}\sum_{k=0}^{k_{\max}} B_k^{n_1-l_1,n_2-l_2}\sum_{p=0}^{\Gamma}\sum_{q=0}^{\Gamma}\left(\Xi^0_{l_1 l_2}\right)_{pq}\\ &\qquad\times\int_{+1}^{\infty}d\xi\int_{-1}^{+1}d\eta\;\xi^{p+k}\;\eta^{q+k_{\max}-k}e^{-\alpha\xi-\beta\eta}\;a_{n_3}[\gamma(\xi+\eta)]\end{aligned} \tag{24}$$

after an elementary integration over the angle ϕ. In the above expression $K_{12} = (R/2)^{n_1+n_2+3}\,\Omega_{l1m1}\,\Omega_{l2m2}$, $k_{\max} = n_1 - l_1 + n_2 - l_2$, α, and β are defined analogously as in Eq. (9) and $\gamma = R\zeta_3/2$. Let us now consider the inner integrals in the above expression and define the auxiliary integrals class:

$$\begin{aligned}&J_\lambda(p,q;\alpha,\beta,\gamma)\\ &\quad=\int_{+1}^{\infty}d\xi\int_{-1}^{+1}d\eta\;\xi^{p}\;\eta^{q}e^{-\alpha\xi-\beta\eta}\;a_\lambda[\gamma(\xi+\eta)].\end{aligned} \tag{25}$$

The above integrals do not separate to a product of one-dimensional integrals and are also very resistant to the numerical integration. However, let us insert the integral representation (12) and change the order of integration so that integrations over ξ and η are performed first. One easily recognizes that the inner integrals are the Mulliken integrals defined in Eqs. (10) and (11) and the integrals (25) can be written as

$$J_\lambda(p,q;\alpha,\beta,\gamma) = \int_0^1 dt\; t^\lambda A_p(\alpha+\gamma t)\; B_q(\beta-\gamma t). \tag{26}$$

Note that, apart from reducing the dimensionality of the integral, we have obtained a form which is very convenient for the numerical integration. The Mulliken integrals are smooth, continuous functions of the real variable with no singularities on the integration line or unwanted oscillatory behavior. Therefore, there is no need to use numerical quadratures with overwhelmingly large number of points. Additionally, the Mulliken integrals can be calculated extremely efficiently in a recursive fashion for arbitrary values of the parameters.

Despite the obvious advantages of the numerical integration of Eq. (26), this approach still has to be justified to some extent. One may ask what is the point of using numerical integration since integrals (26) can be worked out analytically. One can do that, for instance, by inserting in Eq. (26) the explicit expressions for the Mulliken integrals, which are available in the literature [100]. Next, the integral over t can be expressed as a hypergeometric function of two integer parameters and with help of the so-called contiguous relations one can reduce the initial integrals to combinations of the well-known basic functions. This approach seems to be particularly attractive for the Coulomb integrals (when $\zeta_2 = 0$) since, as pointed out by Tai [82], the final explicit expressions contain only elementary functions of the real variables. Therefore, the numerical approach to the integrals (26) seems to be an unwise decision at first glance.

However, the actual situation is more complicated. Taking Eq. (26) as a starting point, we note that the explicit expressions for B_q functions are badly conditioned due to cancellation of two large terms to a relatively small result. That is why computation of B_q from the analytic expressions is unstable and alternate methods need to be utilized [101,115]. This instability propagates further to the integrals (26) and becomes more pronounced as the value of q increases. Nonetheless, with help of the symbolic algebra package, such as *Mathematica*, one can derive explicit expressions for J_λ in order to verify their usefulness. We found that for $\beta \approx \gamma$ the loss of digits is enormous, even when the values of q are not large. Therefore, a prohibitively high arithmetic precision is required to obtain any useful information about the values of J_λ. Taking into consideration the philosophy presented in the Introduction (favoring accuracy over speed within reasonable limits), the above observation seems to state a deadly argument against the analytic approach. In other words, the numerical integration can be understood as a simple way to avoid a severe digital erosion.

For the benchmarking purposes, we show results of the calculation of two integrals, $\widetilde{S}^{1512m}_{1312m}(26;\zeta_1,0,\zeta_3)$ and $\widetilde{S}^{21,18,m}_{7,6,m}(26;\zeta_1,\zeta_1,\zeta_3)$, within the reasonable range of values of the nonlinear parameters ζ_1, ζ_3. We are free to set $R = 1$ since an increase of R results only in scaling of the nonlinear parameters by R (up to a trivial multiplicative constant). All necessary J_λ integrals were calculated numerically using 100 or 200 grid points of the Tanh-Sinh quadrature [124,125] for double and quadruple arithmetic precision, respectively. Under these conditions, J_λ integrals are typically calculated with full precision allowed by the arithmetic.

The integrals, $\widetilde{S}^{1512m}_{1312m}(26;\zeta_1,0,\zeta_3)$ and $\widetilde{S}^{21,18,m}_{7,6,m}(26;\zeta_1,\zeta_1,\zeta_3)$, are the most difficult quantities (in terms of the angular momentum) encountered in the calculation of the Coulomb and hybrid integrals, respectively, including, at most, $7i$ functions. We set $\zeta_2 = \zeta_1$ in the second integral for illustrative purposes; the overall picture changes very slightly when the value of ζ_2 is distorted. The results are presented in Table I for the first integral and in Table II for the second integral. One observes a progressive loss of digits when one of the nonlinear parameters is large and the second is small. This digital erosion is due to the cancellation of large numbers during summations in Eq. (24) and it cannot be avoided in the ellipsoidal coordinates method. The use of quadruple precision improves the situation a lot but it is not sufficient to cope with the most difficult cases. Of course, for lower angular momentum functions the changes are less sharp but the overall trend remains the same. Concluding, our observations signal that the ellipsoidal coordinates method alone is not sufficient to calculate the desired integrals with the prescribed accuracy and need to be supplemented by a different algorithm.

In the present series of papers we do not go into technical details of the implementation, etc., but let us give a short remark on the timings in the present algorithm. The numerical integration of the integrals J_λ typically consumes about a half of the total time necessary to calculate a given shell of integrals.

TABLE I. Calculation of $\widetilde{S}^{15,12,m}_{13,12,m}(26;\zeta_1,0,\zeta_3)$ using the method based on ellipsoidal coordinates. The values of ζ_1, ζ_3 increase along the columns or rows, respectively. The values presented are in the form d − q, which denotes (rounded) decimal logarithms of the relative error obtained in double and quadruple arithmetic precision, respectively. Therefore, these values roughly represent the number of correct significant digits obtained using the present algorithm. Values obtained in quadruple precision were demoted to double precision before the comparison since these are the values used in the actual calculations. The worst result obtained within the possible range of m was chosen in all cases. Reference values were obtained from calculations in extended arithmetic precision of 128 significant digits.

ζ_1/ζ_3	0.1250	0.2500	0.5000	1.0000	2.0000	4.0000	8.0000	16.000	32.000	64.000	128.00	256.00
0.1250	9−16	9−16	8−16	9−16	8−16	7−16	8−16	5−16	1−16	0−13	0−5	0−0
0.2500	8−16	8−16	8−16	8−16	8−16	9−16	7−16	5−16	1−16	0−13	0−5	0−0
0.5000	9−16	8−16	8−16	8−16	8−16	7−16	6−16	5−16	1−16	0−12	0−4	0−0
1.0000	9−16	8−16	9−16	8−16	8−16	7−16	7−16	4−16	0−16	0−12	0−5	0−0
2.0000	8−16	8−16	8−16	9−16	8−16	7−16	8−16	5−16	0−16	0−11	0−4	0−0
4.0000	8−16	8−16	8−16	9−16	7−16	8−16	7−16	5−16	0−16	0−12	0−5	0−0
8.0000	8−16	8−16	8−16	6−16	7−16	8−16	7−16	5−16	1−16	0−14	0−7	0−1
16.000	7−16	7−16	7−16	5−16	5−16	5−16	6−16	7−16	4−16	0−16	0−9	0−3
32.000	4−16	4−16	4−16	3−16	2−16	2−16	1−16	4−16	6−16	0−16	0−11	0−4
64.000	0−16	0−16	0−15	0−14	0−15	0−14	0−14	0−16	2−16	1−16	0−12	0−4
128.00	0−10	0−10	0−8	0−8	0−7	0−7	0−8	0−11	0−14	1−15	0−12	0−4
256.00	0−4	0−4	0−2	0−1	0−1	0−0	0−1	0−4	0−7	0−14	0−12	0−4

Only for the smallest values of the quantum numbers is this ratio higher, but these integrals are very cheap anyway. The remaining time is spent on the lengthy summations in Eq. (24), formation of $\widetilde{I}_{C/H}$, Eqs. (20) and (21), and summation of the initial Clebsh-Gordan expansion to finally arrive at the value of $I_{C/H}$. Therefore, the numerical integration is not connected with a drastic overhead, as might have been initially expected. A faster scheme for the calculation of J_λ shall not result in a significant overall speed-up. Typically, the Coulomb and hybrid integrals are obtained in 1–100 μs per integral, depending on the values of quantum numbers, with hybrid integrals being slightly more expensive.

C. Calculation of the overlaplike integrals by the recursive method

For the calculation of the overlaplike integrals by using the recursive method it is more convenient to introduce different basic integrals, so that the final expressions take a simpler form. Let us note that Eq. (23) can be rewritten as

$$\widetilde{S}^{n_2 l_2 m}_{n_1 l_1 m}(n_3;\zeta_1,\zeta_2,\zeta_3) = \frac{1}{R}\,\Omega_{l_1 m}\Omega_{l_2 m}\langle\varphi^{l_1 m}_{n_1}|\varphi^{l_2 m}_{n_2}\rangle, \tag{27}$$

where

$$\langle\varphi^{l_1 m}_{n_1}|\varphi^{l_2 m}_{n_2}\rangle = \int_0^\infty dr_a \int_{|r_a-R|}^{r_a+R} dr_b\; r_a^{n_1} r_b^{n_2} e^{-\zeta_1 r_a-\zeta_2 r_b} \times P^m_{l_1}(\cos\theta_a)\; P^m_{l_2}(\cos\theta_b)\; a_{n_3}(\zeta_3 r_{1b}). \tag{28}$$

In the second expression we changed the variables from the Cartesian coordinates to the internal coordinate system (r_a,r_b,ϕ) and integrated over the angle. Note that the notation for the nonlinear parameters and for the variable n_3 was suppressed since these quantities do not change during the recursive process. We have to stress that all formulas presented here are valid only for $m > 0$. There is no need to consider

TABLE II. Calculation of $\widetilde{S}^{21,18,m}_{7,6,m}(26;\zeta_1,\zeta_1,\zeta_3)$ using the method based on the ellipsoidal coordinates. The values of ζ_1, ζ_3 increase along the columns or rows, respectively. The values presented are in the form d − q, which denotes (rounded) decimal logarithms of the relative error obtained in double and quadruple arithmetic precision, respectively. Therefore, these values roughly represent the number of correct significant digits obtained using the present algorithm. Values obtained in quadruple precision were demoted to double precision before the comparison since these are the values used in the actual calculations. The worst result obtained within the possible range of m was chosen in all cases. Reference values were obtained from calculations in extended arithmetic precision of 128 significant digits.

ζ_1/ζ_3	0.1250	0.2500	0.5000	1.0000	2.0000	4.0000	8.0000	16.000	32.000	64.000	128.00	256.00
0.1250	0−9	0−10	0−12	0−16	1−16	6−16	7−16	7−16	6−16	6−16	4−16	4−16
0.2500	0−10	0−10	0−13	0−16	2−16	5−16	8−16	7−16	6−16	7−16	4−16	4−16
0.5000	0−10	0−10	0−13	0−16	3−16	6−16	7−16	7−16	6−16	7−16	4−16	4−16
1.0000	0−11	0−11	0−14	0−16	2−16	5−16	7−16	7−16	7−16	7−16	5−16	5−16
2.0000	0−12	0−13	0−15	0−16	2−16	5−16	7−16	6−16	6−16	6−16	5−16	5−16
4.0000	0−14	0−15	0−16	0−16	2−16	4−16	6−16	5−16	6−16	6−16	5−16	5−16
8.0000	0−16	0−16	0−16	0−16	2−16	3−16	4−16	4−16	4−16	4−16	7−16	5−16
16.000	0−16	0−16	0−16	0−16	1−16	1−16	1−16	2−16	2−16	2−16	4−16	3−16
32.000	0−13	0−14	0−13	0−14	0−15	0−15	0−15	0−16	0−16	0−16	0−15	0−14
64.000	0−6	0−6	0−6	0−7	0−7	0−8	0−9	0−9	0−9	0−6	0−5	0−4
128.00	0−0	0−0	0−0	0−0	0−0	0−0	0−1	0−2	0−2	0−4	0−3	0−2

the negative values of m because of the axial symmetry of the integrands.

Generally speaking, to establish a recursive process which is able to increase the values of l_1, l_2, and m, starting with provided values of $\langle\varphi^{00}_{n_1}|\varphi^{00}_{n_2}\rangle$ we need to use the well-known recursion relations for the Legendre polynomials P^m_l. A similar idea was applied by several authors to the calculation of various important matrix elements [78,94–99]. Let us first derive a recursion relation connecting $\langle\varphi^{mm}_{n_1}|\varphi^{mm}_{n_2}\rangle$ with different m by recalling the expression for the Legendre polynomials with $l = m$,

$$P^m_m(\cos\theta) = \frac{(2m)!}{2^m m!}\sin^m\theta, \tag{29}$$

so that

$$P^{m+1}_{m+1}(\cos\theta) = P^m_m(\cos\theta)(2m+1)\sin\theta. \tag{30}$$

By combining two expressions like the above for $\cos\theta_a$ and $\cos\theta_b$ and using the obvious relationship $r_a\sin\theta_a = r_b\sin\theta_b$ one finds

$$\begin{aligned} &P^{m+1}_{m+1}(\cos\theta_a)P^{m+1}_{m+1}(\cos\theta_b) \\ &\quad = P^m_m(\cos\theta_a)P^m_m(\cos\theta_b)(2m+1)^2\frac{r_a}{r_b}\sin^2\theta_a, \end{aligned} \tag{31}$$

and the expression for $\sin^2\theta_a$ in terms of r_a, r_b is elementary. Finally, this leads to the recursion relation for the desired set of integrals

$$\begin{aligned} &\left\langle\varphi^{m+1,m+1}_{n_1}\middle|\varphi^{m+1,m+1}_{n_2}\right\rangle \\ &\quad = \frac{(2m+1)^2}{2R^2}\Big[R^2\langle\varphi^{mm}_{n_1+1}|\varphi^{mm}_{n_2-1}\rangle + R^2\langle\varphi^{mm}_{n_1-1}|\varphi^{mm}_{n_2+1}\rangle \\ &\qquad + \langle\varphi^{mm}_{n_1+1}|\varphi^{mm}_{n_2+1}\rangle - \frac{1}{2}R^4\langle\varphi^{mm}_{n_1-1}|\varphi^{mm}_{n_2-1}\rangle \\ &\qquad - \frac{1}{2}\langle\varphi^{mm}_{n_1+3}|\varphi^{mm}_{n_2-1}\rangle - \frac{1}{2}\langle\varphi^{mm}_{n_1-1}|\varphi^{mm}_{n_2+3}\rangle\Big]. \end{aligned} \tag{32}$$

The second ingredient of the recursive process is a relation that makes it possible to increase the values of l_1 and l_2 independently, starting with the just considered $\langle\varphi^{mm}_{n_1}|\varphi^{mm}_{n_2}\rangle$ integrals. The following recursion relation for the Legendre polynomials is useful:

$$(l-m+1)P^m_{l+1}(x) + (l+m)P^m_{l-1}(x) = (2l+1)xP^m_l(x). \tag{33}$$

If one uses the above relation for $P^m_{l_1}(\cos\theta_a)$ in Eq. (28) and subsequently expresses $\cos\theta_a$ through r_a and r_b from the cosine theorem, the following recursion is obtained:

$$\begin{aligned} &\frac{1}{2R}\left[\langle\varphi^{l_1m}_{n_1+1}|\varphi^{l_2m}_{n_2}\rangle - \langle\varphi^{l_1m}_{n_1-1}|\varphi^{l_2m}_{n_2+2}\rangle + R^2\langle\varphi^{l_1m}_{n_1-1}|\varphi^{l_2m}_{n_2}\rangle\right] \\ &\quad = (l_1-m+1)\langle\varphi^{l_1+1,m}_{n_1}|\varphi^{l_2m}_{n_2}\rangle + (l_1+m)\langle\varphi^{l_1-1,m}_{n_1}|\varphi^{l_2m}_{n_2}\rangle, \end{aligned} \tag{34}$$

which can be used to increase l_1 at cost of n_1 and n_2. A corresponding expression for increasing l_2 can be obtained by repeating the derivation for $P^m_{l_2}(\cos\theta_b)$. Therefore, by using Eq. (34) and its counterpart for the center b, we can build all $\langle\varphi^{l_1m}_{n_1}|\varphi^{l_2m}_{n_2}\rangle$ starting with integrals with $l_1 = l_2 = m$ and higher n_1, n_2.

Having said this, the only thing that remains in question is the calculation of the pertinent integrals $\langle n_1 00|n_2 00\rangle$. Let us return to Eq. (28),

$$\begin{aligned} &\left\langle\varphi^{00}_{n_1}\middle|\varphi^{00}_{n_2}\right\rangle \\ &\quad = \int_0^\infty dr_a\int_{|r_a-R|}^{r_a+R} dr_b\, r_a^{n_1}r_b^{n_2}e^{-\zeta_1 r_a-\zeta_2 r_b}\, a_{n_3}(\zeta_3 r_{1b}), \end{aligned} \tag{35}$$

use the integral representation of a_n, Eq. (12), and reverse the order of integration. By doing so we obtain an equivalent representation of the basic integrals

$$\left\langle\varphi^{00}_{n_1}\middle|\varphi^{00}_{n_2}\right\rangle = \int_0^1 dt\, t^{n_3}\,\Gamma_{n_1n_2}(R;\zeta_1,\zeta_2+t\zeta_3), \tag{36}$$

where Γ_{mn} are the usual overlap integrals between ns-type orbitals,

$$\Gamma_{mn}(R;\zeta_1,\zeta_2) = \int_0^\infty dr_a\int_{|r_a-R|}^{r_a+R} dr_b\, r_a^m r_b^n\, e^{-\zeta_1 r_a-\zeta_2 r_b}. \tag{37}$$

In our approach, the outer integral in (36) is carried out numerically. The arguments for this approach are virtually the same as in the ellipsoidal coordinates method. Roughly speaking, numerical integration serves as a way to avoid numerical instabilities which inevitably appear when the analytic approaches are used. However, now we require a robust scheme for the calculation of Γ_{mn}, so that these integrals can be computed at each point of the grid without a great overhead. In fact, the main advantage of the numerical integration in the ellipsoidal coordinates method was that the integrand in Eq. (26) could be evaluated extremely efficiently and with a strictly controlled precision. On the other hand, the desired algorithm has to preserve a decent accuracy up to large values of m and n (several tens, say). Determination of such an algorithm still presents a challenge from the practical point of view.

The basic integrals Γ_{mn} are well known in the literature. Many authors considered their computation by using several different algorithms which varied in accuracy and speed. Let us note, however, that in the calculation of the integrals (37) the main issue is the numerical stability. The actual expressions for these integrals are not difficult to derive and include only simple elementary functions. Unfortunately, these expressions consist of finite series with terms of alternating signs. When m, n are increased these terms grow exponentially while the sum remains by orders of magnitude smaller. As a result, a gross digital erosion is inevitable. In a large fraction of works which considered calculation of the integrals (37), or used them as a part of different algorithms, the issue of numerical stability was completely disregarded or treated very lightly. The common justification for this fact is that authors were mainly interested in low quantum numbers or devised their algorithms to verify the correctness of the approach more than to perform general calculations.

Let us begin by noting that all integrals (37) can be generated by a consecutive differentiation of Γ_{00} with respect to the nonlinear parameters ζ_1, ζ_2, i.e.,

$$\Gamma_{mn}(R;\zeta_1,\zeta_2) = \left(-\frac{\partial}{\partial\zeta_1}\right)^m\left(-\frac{\partial}{\partial\zeta_2}\right)^n\Gamma_{00}(\zeta_1,\zeta_2), \tag{38}$$

which is, in substance, a trivial case of the so-called shift method of Fernández Rico *et al.* [51–53]. The simplest

integrals Γ_{00} are elementary,

$$\Gamma_{00}(R;\zeta_1,\zeta_2) = \frac{2}{\zeta_1+\zeta_2}\frac{e^{-\zeta_2 R}-e^{-\zeta_1 R}}{\zeta_1-\zeta_2}. \tag{39}$$

It is now convenient to define g_{00} by

$$g_{00}(R;\zeta_1,\zeta_2) = 2\,\frac{e^{-\zeta_2 R}-e^{-\zeta_1 R}}{\zeta_1-\zeta_2}, \tag{40}$$

so that $\Gamma_{00} = g_{00}/(\zeta_1+\zeta_2)$, and the definition of g_{mn} is analogous,

$$g_{mn}(R;\zeta_1,\zeta_2) = \left(-\frac{\partial}{\partial\zeta_1}\right)^m\left(-\frac{\partial}{\partial\zeta_2}\right)^n g_{00}(\zeta_1,\zeta_2). \tag{41}$$

Let us now multiply both sides of Eq. (39) by $\zeta_1+\zeta_2$, rewrite the result in terms of g_{00}, and differentiate both sides m with respect to $-\zeta_1$ and n times with respect to $-\zeta_2$. After some rearrangements, the final result can be written as

$$\Gamma_{mn} = \frac{1}{\zeta_1+\zeta_2}[g_{mn} + m\Gamma_{m-1,n} + n\Gamma_{m,n-1}], \tag{42}$$

where the notation for the nonlinear parameters is suppressed for brevity. The above expression is an inhomogeneous linear recursion relation for Γ_{mn}. Note, that all integrals Γ_{mn} are positive and so are the values of g_{mn}. Therefore, the above recursion relation is completely stable. This approach is reminiscent of the treatment of the one-center integrals by Sack *et al.* [126].

The problem is now reduced to an efficient calculation of g_{mn}. Explicit differentiation is not an option because of similar cancellations as for the initial Γ_{mn} integrals. However, let us observe that g_{00} can also be rewritten as

$$g_{00}(\zeta_1,\zeta_2) = 2Re^{-\zeta_1 R}M[1,2,(\zeta_1-\zeta_2)R], \tag{43}$$

where $M(a,b,z)$ is the confluent hypergeometric function [106] (denoted as ${}_1F_1$ by some authors). By using two differentiation formulas for $M(a,b,z)$,

$$\frac{\partial^n}{\partial z^n}M(a,b,z) = \frac{(a)_n}{(b)_n}M(a+n,b+n,z), \tag{44}$$

$$\frac{\partial^n}{\partial z^n}[e^{-z}M(a,b,z)] = (-1)^n\frac{(b-a)_n}{(b)_n}e^{-z}M(a,b+n,z), \tag{45}$$

one easily arrives at the new formula for g_{mn},

$$g_{mn}(\zeta_1,\zeta_2) = \frac{2m!n!}{(m+n+1)!}\,e^{-\zeta_1 R}\,R^{m+n+1} \times M[1+n,2+m+n,(\zeta_1-\zeta_2)R]. \tag{46}$$

At this point the problem can be considered to be solved because methods of calculation of $M(a,b,z)$ for arbitrary real (or even complex) values of the parameters a, b, and z exist. Let us note that here we deal with an exceptionally special case of $M(a,b,z)$, with both a and b being strictly positive integers, and additionally $b > a$ always holds. Moreover, we can use the symmetry of the initial integrals, $\langle\varphi^{00}_{n_1}|\varphi^{00}_{n_2}\rangle = \langle\varphi^{00}_{n_2}|\varphi^{00}_{n_1}\rangle$, in order to impose the restriction $\zeta_1 \geqslant \zeta_2$, which gives $z \geqslant 0$. All these conditions signal that we should design a dedicated procedure for the calculation of $M(a,b,z)$ in this special case and avoid using general algorithms which are drastically more complicated and involve a large computational overhead. In the Appendix we present a recursive method which is able to calculate $M(a,b,z)$ in our special case with a decent speed, at the same time preserving full accuracy allowed by the arithmetic.

In Tables III and IV we present results of the benchmark calculations for the same representative integrals, $\widetilde{S}^{1512m}_{1312m}(26;\zeta_1,0,\zeta_3)$ and $\widetilde{S}^{21,18,m}_{7,6,m}(26;\zeta_1,\zeta_1,\zeta_3)$, as in the previous section. We use the same numerical quadrature as before and typically a machine precision is obtained in Eq. (36). One sees that the recursive algorithm fails completely, even in the quadruple arithmetic precision, when nonlinear parameters are both small. On the other hand, as they get large the accuracy gradually improves, which is exactly the opposite behavior to the one found in the ellipsoidal method. Therefore,

TABLE III. Calculation of $\widetilde{S}^{15,12,m}_{13,12,m}(26;\zeta_1,0,\zeta_3)$ using the recursive method. The values of ζ_1, ζ_3 increase along the columns or rows, respectively. The values presented are in the form d − q, which denotes (rounded) decimal logarithms of the relative error obtained in double and quadruple arithmetic precision, respectively. Therefore, these values roughly represent the number of correct significant digits obtained using the present algorithm. Values obtained in quadruple precision were demoted to double precision before the comparison since these are the values used in the actual calculations. The worst result obtained within the possible range of m was chosen in all cases. Reference values were obtained from calculations in extended arithmetic precision of 128 significant digits.

ζ_1/ζ_3	0.1250	0.2500	0.5000	1.0000	2.0000	4.0000	8.0000	16.000	32.000	64.000	128.00	256.00
0.1250	0−0	0−0	0−0	0−0	0−0	0−5	0−11	1−16	4−16	5−16	1−16	0−11
0.2500	0−0	0−0	0−0	0−0	0−0	0−5	0−11	1−16	4−16	5−16	1−16	0−11
0.5000	0−0	0−0	0−0	0−0	0−0	0−5	0−11	1−16	4−16	5−16	1−16	0−11
1.0000	0−0	0−0	0−0	0−0	0−0	0−5	0−11	1−16	4−16	5−16	1−16	0−11
2.0000	0−0	0−0	0−0	0−0	0−0	0−6	0−10	0−14	4−16	4−16	0−14	0−11
4.0000	0−6	0−6	0−6	0−6	0−6	0−5	0−11	1−16	3−16	4−16	1−16	0−12
8.0000	0−12	0−12	0−12	0−12	0−10	0−12	1−16	3−16	3−16	2−16	1−16	0−12
16.000	1−16	1−16	1−16	1−16	0−14	1−16	1−16	2−16	2−16	1−16	0−15	0−11
32.000	4−16	4−16	4−16	4−16	4−16	3−16	3−16	5−16	6−16	2−16	1−16	0−14
64.000	5−16	5−16	5−16	5−16	4−16	3−16	4−16	7−16	9−16	6−16	1−16	0−15
128.00	1−16	1−16	1−16	1−16	0−14	1−16	1−16	1−16	4−16	3−16	0−16	0−13
256.00	0−12	0−12	0−12	0−12	0−10	0−12	0−12	0−12	0−13	0−13	0−14	0−12

TABLE IV. Calculation of $\widetilde{S}^{21,18,m}_{7,6,m}(26;\zeta_1,\zeta_1,\zeta_3)$ using the recursive method. The values of ζ_1, ζ_3 increase along the columns or rows, respectively. The values presented are in the form d − q, which denotes (rounded) decimal logarithms of the relative error obtained in double and quadruple arithmetic precision, respectively. Therefore, these values roughly represent the number of correct significant digits obtained using the present algorithm. Values obtained in quadruple precision were demoted to double precision before the comparison since these are the values used in the actual calculations. The worst result obtained within the possible range of m was chosen in all cases. Reference values were obtained from calculations in extended arithmetic precision of 128 significant digits.

ζ_1/ζ_3	0.1250	0.2500	0.5000	1.0000	2.0000	4.0000	8.0000	16.000	32.000	64.000	128.00	256.00
0.1250	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0
0.2500	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0
0.5000	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0
1.0000	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0
2.0000	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0
4.0000	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0	0−0
8.0000	0−5	0−5	0−5	0−5	0−5	0−5	0−5	0−6	0−6	0−6	0−5	0−4
16.000	0−12	0−12	0−12	0−12	0−12	0−12	0−12	0−13	0−13	0−13	0−12	0−11
32.000	6−16	6−16	6−16	6−16	6−16	6−16	6−16	6−16	7−16	7−16	4−16	0−14
64.000	8−16	8−16	8−16	8−16	8−16	8−16	8−16	8−16	9−16	10−16	6−16	0−15
128.00	4−16	4−16	4−16	4−16	4−16	4−16	4−16	4−16	6−16	7−16	2−16	0−14

two methods presented in this paper can be considered fully complementary and together are able to cover a sufficiently large range of the nonlinear parameters. Outside this range, hybrid integrals are usually very small and are typically neglected in advance by the Schwarz screening technique or a similar scheme. Coulomb integrals with bigger values of the nonlinear parameters may still be non-negligible. However, they can be computed with different standard techniques, such as the multipole expansion. It is mandatory for a general program to include such a method as an option.

IV. CONCLUSIONS

Concluding, we derived new expressions for the Coulomb and hybrid integrals over the STOs, with no restrictions on the values of the quantum numbers, starting by a direct integration over coordinates of the second electron. In this way the desired integrals reduce to combinations of ordinary overlap integrals and a set of the so-called overlaplike integrals. These basic integrals are evaluated by using two distinct methods: direct integration in the ellipsoidal coordinate system or with a recursive scheme for increasing angular momenta in the integrand. One of the biggest problems in actual computations is numerical stability of the resulting algorithms. Many formulations available in the literature contain numerically badly conditioned expressions which introduce a significant loss of digits when evaluated in a finite arithmetic precision. We show how these instabilities can be avoided if a simple, one-dimensional numerical integration is used instead. We discuss that this numerical approach introduces an acceptable computational overhead due to well-behaved and simple forms of the integrands. We also show that the remaining numerical instabilities can be easily controlled. Extensive numerical tests are presented, verifying the usefulness and applicability of the method.

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APPENDIX: CALCULATION OF $M(a,b,z)$ FOR $a,b \in \mathbb{Z}_+, b > a, z \geqslant 0$

Let us start by recalling some of the useful formulas obeyed by $M(a,b,z)$. The first one is the Gautschi representation of the continued fraction (GCF) [127], which states that

$$\frac{M(a+1,b,z)}{M(a,b,z)} = 1 + \frac{z}{a}\sum_{k=0}^{\infty} p_k,$$

$$p_0 = 1, \quad p_k = \prod_{i=1}^{k} r_i,$$

$$r_0 = 0, \quad r_k = -\frac{a_k(1+r_{k-1})}{1+a_k(1+r_{k-1})},$$

$$a_k = \frac{(a+k)z}{(b-z+k-1)(b-z+k)}. \tag{A1}$$

The second useful expression is the recursion relation which allows to increase the value of a at constant b:

$$(b-a)M(a-1,b,z) + (2a-b+z)M(a,b,z) - aM(a+1,b,z) = 0. \tag{A2}$$

The region $a,b \in \mathbb{Z}_+$, $b > a$, $z \geqslant 0$ needs to be divided into three subregions and different algorithms have to be used in each of them. They are as follows.

(i) $b \geqslant 2a + z$. One first uses GCF, Eq. (A1), in order to obtain the ratio $M(a+1,b,z)/M(a,b,z)$ for the maximal desired b and $a = \lceil (b-z)/2 \rceil$ ($\lceil * \rceil$ is the ceiling function). The recursion (A2) can be rewritten as

$$r_{a-1} = \frac{b-a}{ar_a + b - 2a - z}, \tag{A3}$$

where $r_a = M(a+1,b,z)/M(a,b,z)$. This recursion is then carried out downward, starting with the value of the ratio obtained from GCF, until r_0 is reached. Since $M(0,b,z) = 1$, it turns out that $r_0 = M(1,b,z)$ and other values can be obtained by using the definition of r_a, e.g., $M(2,b,z) = r_1 M(1,b,z)$.

(ii) $b < 2a + z$, $b \geqslant z$. Again, the relation (A2) is transformed into a Miller-like two-step recursion,

$$r_a = \frac{b-a}{a}\frac{1}{r_{a-1}} + 2 + \frac{z-b}{a}, \tag{A4}$$

with r_a being defined in the same way as previously. Starting with an arbitrary value of r_0, this recursion is carried out upward up to the line $a = b$ (corresponding to r_{b-1}). Using the exact relationship $M(b,b,z) = e^z$, one finds that actual values of $M(a,b,z)$ can be reconstructed as $M(b-1,b,z) = M(b,b,z)/r_{b-1} = e^z/r_{b-1}$, $M(b-2,b,z) = M(b-1,b,z)/r_{b-2}$, etc., until the value of $M(1,b,z)$ is reached.

(iii) $b < 2a + z$, $b < z$. This is the so-called anomalous convergence region of GCF; i.e., the expression (A1) converges to the wrong result [127] and therefore cannot be used. However, in this region the initial upward recursion (A2) is totally stable since all terms in (A2) are positive. The starting (exact) values are

$$M(0,b,z) = 1, \tag{A5}$$

$$M(1,b,z) = (b-1)e^z a_{b-2}(z), \tag{A6}$$

where a_n are given by Eq. (12). The second relationship breaks down when $b = 1$ but in this case we obtain independently $M(1,1,z) = e^z$, as noted beforehand.

Let us also add in passing that the power series expansion of $M(a,b,z)$ around $z = 0$ can additionally be used for small z,

$$M(a,b,z) = \sum_{s=0}^{\infty} \frac{(a)_s}{(b)_s s!} z^s, \tag{A7}$$

since it typically converges very fast in the vicinity of the origin, $z \approx 0$. A similar conclusion holds for the asymptotic expansion of $M(a,b,z)$ as z is large. Remarkably, when the values of $M(a,b,z)$ are calculated as described in this appendix, no loss of digits is observed, and thus $\langle \varphi_{n_1}^{00} | \varphi_{n_2}^{00} \rangle$ can be obtained with full precision up to very large values of n_1 and n_2.

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I. SUPPLEMENTAL MATERIAL FOR PAPER I

Let us consider an atomic integral

$$I = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \, \chi_{n_1 l_1}(\mathbf{r}_1;\zeta_1)\chi_{n_2 l_2}(\mathbf{r}_1;\zeta_2)\frac{1}{r_{12}}\chi_{n_3 l_3}(\mathbf{r}_2;\zeta_3)\chi_{n_4 l_4}(\mathbf{r}_2;\zeta_4), \tag{1}$$

where all orbitals are located at the same point of space. By using the Laplace expansion for the term $\frac{1}{r_{12}}$ and integrating over the angular coordinates of both electrons one gets

$$\begin{aligned} I = (-1)^{m_1+m_3}&\sqrt{\prod_{i=1}^{4}(2l_i+1)}\sum_L \begin{pmatrix} l_1 & L & l_2 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_3 & L & l_4 \\ 0 & 0 & 0 \end{pmatrix} \\ &\times \left[I_L^{>}(n_{12}+2, n_{34}+2; \zeta_{12}, \zeta_{34}) + I_L^{<}(n_{12}+2, n_{34}+2; \zeta_{12}, \zeta_{34})\right] \\ &\times \sum_{M=-L}^{L}(-1)^M \begin{pmatrix} l_1 & L & l_2 \\ -m_1 & -M & m_2 \end{pmatrix}\begin{pmatrix} l_3 & L & l_4 \\ -m_3 & M & m_4 \end{pmatrix}, \end{aligned} \tag{2}$$

where $n_{12} = n_1 + n_2$, $\zeta_{12} = \zeta_1 + \zeta_2$ and the same notation is used for the second electron. The summation over L in the above expression is finite *i.e.* only terms with $\max(|l_1 - l_2|, |l_3 - l_4|) \le L \le \min(l_1 + l_2, l_3 + l_4)$ survive. Let us first consider the integral $I_L^{>}$ which takes the form

$$I_L^{>}(n_1, n_2; \alpha_1, \alpha_2) = \int_0^\infty dr_1 \, r_1^{n_1+L} e^{-\alpha_1 r_1} \int_{r_1}^\infty dr_2 \, r_2^{n_2-L-1} e^{-\alpha_2 r_2}, \tag{3}$$

where the notation for the parameters was simplified for better readability. This integral can be integrated by using elementary methods to give

$$I_L^{>}(n_1, n_2; \alpha_1, \alpha_2) = \frac{\alpha_2^{L-n_2}(n_2 - L - 1)!}{(\alpha_1+\alpha_2)^{n_1+L+1}} \times \sum_{j=0}^{n_2-L-1} \frac{(n_1+L+j)!}{j!}\left(\frac{\alpha_2}{\alpha_1+\alpha_2}\right)^j. \tag{4}$$

Note all terms present in the above sum are positive and thus no cancellation of huge numbers to a relatively small result can occur. The above expression can be put even in a more compact form by using the Pochhammer symbols.

Let us now pass to the second class of integrals ($I_L^{<}$) which are defined as

$$I_L^{<}(n_1, n_2; \alpha_1, \alpha_2) = \int_0^\infty dr_1 \, r_1^{n_1-L-1} e^{-\alpha_1 r_1} \int_0^{r_1} dr_2 \, r_2^{n_2+L} e^{-\alpha_2 r_2}. \tag{5}$$

In some works, the first step to bring the above integrals into a closed form is to manipulate the integration range in the inner integral by inserting an obvious identity $\int_0^{r_1} = \int_0^\infty - \int_{r_1}^\infty$. The advantage of this idea is that all resulting integrals are solved immediately in the same way as $I_L^{>}$. However, for some combinations of α_2 and r_1 the two resulting integrals are nearly equal in magnitude. Therefore, subtraction will cause a significant loss of accuracy. This effect is particularly considerable when the values of the quantum numbers are large.

In the alternative approach, the integration variable in the inner integrand of Eq. (5) is changed to $t = r_2/r_1$. If the order of integration is reversed, the integration over r_1 can be carried out easily and one is left with the following one-dimensional integration

$$I_L^{<}(n_1, n_2; \alpha_1, \alpha_2) = (n_1 + n_2)! \int_0^1 dt \, \frac{t^{n_2+L}}{(\alpha_1 + \alpha_2 t)^{n_1+n_2+1}}. \tag{6}$$

The above integrand is a rational function and the integration can be carried out by using general methods. Taking into account that the relationship $L \le n_2$ always holds, the final result can be cast into the form

$$I_L^{<}(n_1, n_2; \alpha_1, \alpha_2) = \frac{1}{\alpha_1}\frac{(n_2+L)!(n_1-L-1)!}{(\alpha_1+\alpha_2)^{n_1+n_2}} \sum_{k=0}^{n_1-L-1}\binom{n_1+n_2}{n_1-L-1-k}\left(\frac{\alpha_2}{\alpha_1}\right)^k. \tag{7}$$

The above summation includes only terms with positive signs and therefore the whole procedure is completely stable. Moreover, no special functions or infinite summations are required as contrasted to some of the formulations available in the literature.

Paper II

"Reexamination of the calculation of two-center, two-electron integrals over Slater-type orbitals. II. Neumann expansion of the exchange integrals"

Michał Lesiuk and Robert Moszyński

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Commentary

In the second paper of the triptych, calculation of the exchange integrals over STOs is considered. The method of choice in this context is based on the Neumann expansion of the interaction potential. Unfortunately, this expansion is infinite in the general case and truncates only for special combinations of the screening constants. This poses an additional problem for the calculation of the basic quantities - apart from the stability with respect to the quantum numbers and exponents of the orbitals, one additionally has to assure that the method is stable with respect to the order of the expansion. This is the reason why the exchange integrals are widely considered to be the most difficult quantities appearing in the two-centre problem.

The most appealing aspect of the Neumann expansion is that the complicated six-dimensional integrals are automatically rewritten as a sum of the one- and two-dimensional integrations. The lower-dimensional quantities are much simpler to control in terms of numerical stability. In fact, the initial exchange integrals are dependent on many variables - quantum numbers and screening constants of four orbitals in the integrand. This gives a total of twelve integer parameters and four

real (non-negative) parameters. After the Neumann expansion is applied, the most complicated quantity depends only on two real parameters and four integer parameters. Some of the latter can be further eliminated rather straightforwardly. This makes fully analytic approaches much more reasonable.

This point of view permeates Paper II where we pursue the analytic approach advocated in several previous works of other authors. Our main contribution is to derive series expansions which are applicable in situations where other known methods fail. As an example let us consider the basic quantity $L_\mu(\alpha)$ defined by Eq. (7) in Paper II (with $p = \sigma = 0$). It can be shown that the analytic expressions for $L_\mu(\alpha)$ involve drastic cancellations for small α rendering them useless in this regime. It is then a natural idea to derive a small α series expansion for $L_\mu(\alpha)$ which supplements the existing techniques. Unfortunately, it is not trivial to obtain such an expansion and many standard techniques (integration by parts etc.) fail in this case. Our idea is to derive first a differential equation obeyed by $L_\mu(\alpha)$ with α as a variable. Having this differential equation the required series expansion in α is obtained relatively straightforwardly by employing the Frobenius method. Crucially, the coefficients in the expansion are always given by simple recursions, facilitating an efficient implementation.

This basic idea is explored in Paper II for many basic quantities appearing in the Neumann expansion. Moreover, with the help of the differential equation we can also derive large α expansions which are superior in terms of speed within their range of applications. As a supplement, we additionally proposed a new numerical scheme with one-dimensional integration replacing the most time-consuming analytic evaluations. Finally, we performed extensive numerical tests to show that the new method are complementary to the standard techniques and greatly improve the range of applicability of the Neumann expansion of the exchange integrals.

Reexamination of the calculation of two-center, two-electron integrals over Slater-type orbitals. II. Neumann expansion of the exchange integrals

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In this paper we consider the calculation of two-center exchange integrals over Slater-type orbitals (STOs). We apply the Neumann expansion of the Coulomb interaction potential and consider calculation of all basic quantities which appear in the resulting expression. Analytical closed-form equations for all auxiliary quantities have already been known but they suffer from large digital erosion when some of the parameters are large or small. We derive two differential equations which are obeyed by the most difficult basic integrals. Taking them as a starting point, useful series expansions for small parameter values or asymptotic expansions for large parameter values are systematically derived. The resulting expansions replace the corresponding analytical expressions when the latter introduce significant cancellations. Additionally, we reconsider numerical integration of some necessary quantities and present a new way to calculate the integrand with a controlled precision. All proposed methods are combined to lead to a general, stable algorithm. We perform extensive numerical tests of the introduced expressions to verify their validity and usefulness. Advances reported here provide methodology to compute two-electron exchange integrals over STOs for a broad range of the nonlinear parameters and large angular momenta.

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I. INTRODUCTION

In the first paper of the series [1] (denoted as Paper I further in the text), we have discussed calculation of the two-electron Coulomb and hybrid integrals over Slater-type orbitals (STOs). The remaining obstacle in the calculations for the diatomic molecules is an accurate determination of the exchange integrals. These quantities are widely considered to be the most difficult among the two-center integrals. There exists a broad literature on this topic with several seminal works written in 1950s and 1960s or even earlier. In this introduction let us mention briefly the available methods for the calculation of the exchange integrals, concentrating solely on the Neumann expansion method, which has probably the biggest potential of being successful for our purposes.

The first comprehensive scheme utilizing the Neumann expansion approach was given by Ruedenberg and co-workers who rewrote the expressions in terms of the charge distributions on both centers [2,3] and used a simple one-dimensional numerical quadrature [4,5] to avoid analytic integration. A complete recursive scheme which enabled analytical calculation of all auxiliary quantities along with tabulation of some integrals was given in the book of Kotani [6]. Shortly thereafter, Harris [7] introduced significant simplifications in the calculation of some basic integrals by invoking the theory of spherical Bessel functions. Methodology based on the Neumann expansion was then progressively refined by many authors. Some changes were introduced which were aimed at improving the efficiency or accuracy of the algorithms and making the final expressions more transparent and general [8–12]. Importantly, Maslen and Trefry [13] derived explicit analytical expressions for all basic quantities appearing in the Neumann expansion by using the hypergeometric function approach. More or less at the same time the limitations of the available expressions were recognized and a new recursive scheme was proposed by Fernández Rico and co-workers [14]. More recently, Harris pursued the approach of Maslen and Trefry based on the analytical expressions and introduced considerable simplifications and several new expressions which allow more stable calculations of several auxiliary quantities [15]. In this paper we recall some of the works cited above to illuminate the differences and the advantages of the derived expressions compared to those available in the literature.

The paper is organized as follows. In Sec. II we introduce the notation and present all basic quantities that need to be calculated. In Sec. III we present analytic expressions available in the literature. We put special emphasis on their numerical stability and other practical issues. In Sec. IV we derive a differential equation which is obeyed by the first important function family L_μ. By using it, we introduce two new methods of calculations for large or small values of the parameters and discuss a general method of evaluation which is a combination of three analytical methods. Once the problem of the L_μ functions is solved, in Sec. V we move to the calculation of the most important quantities W_μ. We present derivation of the differential equation obeyed by these functions. Next, new methods for calculation of W_μ are introduced. In Sec. VI we introduce a seminumerical method for calculation of the W_μ functions. We also discuss a general algorithm for calculation of W_μ, which is a combination of several known methods. Finally, in Sec. VII we conclude our paper.

In the paper we rely on the known special functions to simplify the derivations and the final formulas. Our convention for all special functions appearing below is the same as in Ref. [16].

II. PRELIMINARIES

In this paper, we consider calculation of two-center exchange integrals in the form

$$(ab|a'b') = \int d\mathbf{r}_1 \int d\mathbf{r}_2\, \chi_a^*(\mathbf{r}_1)\chi_b(\mathbf{r}_1)\frac{1}{r_{12}}\chi_{a'}^*(\mathbf{r}_2)\chi_{b'}(\mathbf{r}_2), \qquad (1)$$

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where r_{12} denotes the interelectron distance. For details of the notation, see the Preliminaries section in Paper I.

The Neumann expansion of $1/r_{12}$ is defined by the formula [2]

$$\frac{1}{r_{12}} = \frac{2}{R}\sum_{\mu=0}^{\infty}\sum_{\sigma=-\mu}^{\mu}(-1)^{\sigma}(2\mu+1)\left[\frac{(\mu-|\sigma|)!}{(\mu+|\sigma|)!}\right]^2 P_{\mu}^{|\sigma|}(\xi_<)Q_{\mu}^{|\sigma|}(\xi_>)P_{\mu}^{|\sigma|}(\eta_1)P_{\mu}^{|\sigma|}(\eta_2)e^{i\sigma(\phi_1-\phi_2)}, \tag{2}$$

where $\xi_< = \min(\xi_1,\xi_2)$ and $\xi_> = \max(\xi_1,\xi_2)$, and other quantities were defined in Paper I. By inserting the above expression into Eq. (1), making use of Eqs. (7)–(9) in Paper I, and carrying out the integration over the angles ϕ_1 and ϕ_2, one arrives at the formula

$$(ab|a'b') = \frac{8}{R}K_{ab}K_{a'b'}\delta_{M_1,-M_2}(-1)^{\sigma}\sum_{k_1=0}^{k_1^{\max}}B_{k_1}^{n_1-l_1,n_2-l_2}\sum_{k_2=0}^{k_2^{\max}}B_{k_2}^{n_3-l_3,n_4-l_4}\sum_{p_1,q_1=0}^{\Gamma_1}\left(\Xi_{l_1l_2}^{M_1}\right)_{p_1q_1}\sum_{p_2,q_2=0}^{\Gamma_2}\left(\Xi_{l_3l_4}^{M_2}\right)_{p_2q_2}$$
$$\times\sum_{\mu=\sigma}^{\infty}(2\mu+1)W_{\mu}^{\sigma}(p_1+k_1,p_2+k_2,\alpha_1,\alpha_2)i_{\mu}^{\sigma}\left(q_1+k_1^{\max}-k_1,\beta_1\right)i_{\mu}^{\sigma}\left(q_2+k_2^{\max}-k_2,\beta_2\right), \tag{3}$$

where δ_{ij} is the Kronecker delta, K_{ab} were defined in Paper I, and $\sigma = |M_1| = |M_2|$ is restricted to the regime $\sigma \geqslant 0$. In the above equation a number of new quantities were introduced. We follow the notation advocated by Harris [15] and others for η integration,

$$i_{\mu}^{\sigma}(q,\beta) = \frac{(-1)^{\mu}}{2}\frac{(\mu-\sigma)!}{(\mu+\sigma)!}\int_{-1}^{+1}d\eta\, P_{\mu}^{|\sigma|}(\eta)(1-\eta^2)^{\sigma/2}\eta^q\, e^{-\beta\eta}, \tag{4}$$

and for ξ integration,

$$W_{\mu}^{\sigma}(p_1,p_2,\alpha_1,\alpha_2) = w_{\mu}^{\sigma}(p_1,p_2,\alpha_1,\alpha_2) + w_{\mu}^{\sigma}(p_2,p_1,\alpha_2,\alpha_1), \tag{5}$$

$$w_{\mu}^{\sigma}(p_1,p_2,\alpha_1,\alpha_2) = \int_1^{\infty}d\xi_1\, Q_{\mu}^{\sigma}(\xi_1)\left(\xi_1^2-1\right)^{\sigma/2}\xi_1^{p_1}e^{-\alpha_1\xi_1}\int_1^{\xi_1}d\xi_2\, P_{\mu}^{\sigma}(\xi_2)\left(\xi_2^2-1\right)^{\sigma/2}\xi_2^{p_2}e^{-\alpha_2\xi_2}. \tag{6}$$

The series in Eq. (3) is, in general, infinite. However, it is convergent for all physically acceptable values of the nonlinear parameters, namely $\alpha_1 \geqslant 0, \alpha_2 \geqslant 0, |\beta_1| \leqslant \alpha_1, |\beta_2| \leqslant \alpha_2$. The rate of convergence depends critically on the values of β. The smaller the $|\beta|$ are, the faster the ellipsoidal expansion converges. In fact, in the limit of $\beta_1 = 0$ or $\beta_2 = 0$ it becomes finite by the virtue of $i_{\mu}^{\sigma}(q,\beta)$ integrals, which we discuss further. Convergence of the Neumann expansion has been studied by several authors and there is a general agreement that at most several tens of terms are sufficient to converge all non-negligible integrals to the prescribed accuracy [8,11]. The "divergence" of the Neumann expansion reported by other authors [17] is only apparent and results solely from the inaccuracies in calculation of the individual terms.

Let us not discuss the calculation of the $i_{\mu}^{\sigma}(q,\beta)$ functions, Eq. (4), which arise from the integration over η_1 and η_2 in Eq. (3). Efficient and accurate recursive formulas that allow their calculation have been known since the 1960 paper of Harris [7]. These expressions were progressively refined by many authors [10,11,13,15]. Therefore, we refer to these papers for methods of computation of $i_{\mu}^{\sigma}(q,\beta)$ and consider this problem as entirely solved for the present purposes.

III. CLOSED-FORM ANALYTICAL FORMULAS FOR THE ξ_1, ξ_2 INTEGRATION

The problem of integration over ξ_1 and ξ_2, i.e., accurate calculation of $W_{\mu}^{\sigma}(p_1,p_2,\alpha_1,\alpha_2)$ functions defined in Eq. (5), is the most important problem in practical utilization of the ellipsoidal expansion. As mentioned in the Introduction, explicit analytical expressions for these functions were derived by Maslen and Trefry [13]. In this section let us recall their formulas and introduce a number of new quantities.

Two new important auxiliary functions need to be defined:

$$L_{\mu}^{\sigma}(p,\alpha) = \frac{(\mu-\sigma)!}{(\mu+\sigma)!}\int_1^{\infty}d\xi\, Q_{\mu}^{\sigma}(\xi)\xi^p(\xi^2-1)^{\sigma/2}e^{-\alpha\xi} \tag{7}$$

and

$$k_{\mu}^{\sigma}(p,\alpha) = \frac{(\mu-\sigma)!}{(\mu+\sigma)!}\int_1^{\infty}d\xi\, P_{\mu}^{\sigma}(\xi)\xi^p(\xi^2-1)^{\sigma/2}e^{-\alpha\xi}. \tag{8}$$

The following recursion formula was presented by Harris [7] and results from the connections of $k_{\mu}^{\sigma}(p,\alpha)$ with the modified spherical Bessel functions:

$$k_{\mu+1}^{0}(0,\alpha) = \frac{2\mu+1}{\alpha}k_{\mu}^{0}(0,\alpha) + k_{\mu-1}^{0}(0,\alpha). \tag{9}$$

This recurrence requires two starting values, $k_0^0(0,\alpha) = k_{-1}^0(0,\alpha) = e^{-\alpha}/\alpha$, and it is stable for all relevant values of α since all terms on right-hand side always have the same sign. Expressions that can be used to build $k_{\mu}^{\sigma}(p,\alpha)$ with nonzero values of p and σ are derived by inserting appropriate recursion formulas for the Legendre functions [16]. The working formulas read

$$k_{\mu}^{\sigma}(p+1,\alpha) = \frac{(\mu-\sigma)k_{\mu-1}^{\sigma}(p,\alpha) + (\mu+\sigma+1)k_{\mu+1}^{\sigma}(p,\alpha)}{2\mu+1} \tag{10}$$

and

$$k_\mu^{\sigma+1}(p,\alpha) = \frac{k_{\mu-1}^{\sigma}(p,\alpha) - k_{\mu+1}^{\sigma}(p,\alpha)}{2\mu+1} \tag{11}$$

and are also completely stable for all acceptable values of α. Calculation of $L_\mu^\sigma(p,\alpha)$ is much more troublesome. The analytical formula was presented by Maslen and Trefry [13],

$$L_\mu^\sigma(p,\alpha) = \sum_s^{\mu+\sigma} \mathcal{A}_s^{\mu\sigma} L_0^0(p+s,\alpha) + \sum_s^{\mu+\sigma-1} \mathcal{B}_s^{\mu\sigma} A_{p+s}(\alpha), \tag{12}$$

with

$$\mathcal{A}_s^{\mu\sigma} = (-1)^{(\mu+\sigma-s)/2} \frac{(\mu-\sigma+s-1)!!}{s!(\mu+\sigma-s)!!}, \tag{13}$$

$$\mathcal{B}_s^{\mu\sigma} = \sum_{j=0}^{(\mu+\sigma-s-1)/2} \frac{(-1)^{j+1}(2\mu-2j-1)!!}{(\mu+\sigma-s-2j)(\mu+\sigma-2j)!(2j)!!}, \tag{14}$$

where !! denotes the double factorial function. The coefficients $\mathcal{A}_s^{\mu\sigma}$ vanish unless $\mu+\sigma-s$ is even, and $\mathcal{B}_s^{\mu\sigma}$ are nonzero if and only if $\mu+\sigma-s$ is odd. The quantities $A_n(\alpha)$ are well known [18,19] and were defined in Paper I.

The remaining necessary formula for $L_0^0(p,\alpha)$ can be obtained by direct integration. The result reads (note the sign error in the original formula [13])

$$L_0^0(p,\alpha) = \frac{1}{2}\Bigg[(-1)^{p+1} E_1(2\alpha) A_p(-\alpha) + [\gamma_E + \ln(2\alpha)] A_p(\alpha) + \frac{p!e^{-\alpha}}{\alpha^{p+1}} \sum_{r=1}^{p-1} \mathcal{L}_{pr} \frac{\alpha^r}{r!}\Bigg], \tag{15}$$

where E_1 is the generalized exponential integral function [16], γ_E is the Euler-Mascheroni constant, and $\mathcal{L}_{pr}$ are numerical coefficients given in the simplified form by Harris [15]:

$$\mathcal{L}_{pr} = \sum_j^r \left(\frac{1}{j+p-r} - \frac{1}{j}\right) \sum_{k=j}^r (-1)^{r-k} 2^k \binom{r}{k}. \tag{16}$$

Once the integrals $L_\mu^\sigma(p,\alpha)$ are calculated, the final formula for $w_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$, presented by Maslen and Trefry [13] and simplified considerably by Harris [15], is as follows:

$$w_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2) = \left[\frac{(\mu+\sigma)!}{(\mu-\sigma)!}\right]^2 \Bigg[L_\mu^\sigma(p_1,\alpha_1) k_\mu^\sigma(p_2,\alpha_2) - \sum_s^\mu \mathcal{A}_s^{\mu\sigma} \sum_{j=0}^{p_2+s} \frac{(p_2+s)!}{j!\alpha_2^{p_2+s}} L_\mu^\sigma(p_1+j,\alpha_1+\alpha_2) \Bigg]. \tag{17}$$

Since closed-form analytical formulas exist for all basic quantities involved in the calculation of the integrals, it seems that the problem is solved. This is true, however, only in an arbitrary arithmetic precision environment such as *Mathematica* [20]. Unfortunately, this kind of environment is too slow to support large-scale calculations in the basis sets close to the saturation. For practical purposes, we require a theory that allows calculations in a numerically stable way, presumably in the double or at most quadruple arithmetic precision, for a large range of parameter values and high angular momenta.

Reasons for the observed numerical instabilities were partially recognized by Maslen and Trefry [13] and analyzed in detail by Harris [15]. The latter paper should be consulted for a more elaborate study of the numerical instabilities. We give only a superficial overview of the problem.

Two the most important working formulas, Eqs. (12) and (17), are both numerically badly conditioned. Equation (12) is unstable for small values of α when μ and/or p are moderate or large. This happens due to large cancellation occurring between the first and the second terms, which are both large, nearly equal, and of opposite signs. Our numerical tests have shown that this formula provides a sufficient level of accuracy for all practically required μ, p, and σ only if $\alpha \geqslant 3$. This agrees more or less with the conclusion of Maslen and Trefry. Unfortunately, typical basis sets give rise to the integrals which require α to be considerably smaller than that. Therefore, Eq. (12) alone is not sufficient to calculate all necessary integrals with a controlled precision. Thus, a different method has to be devised for the small α regime.

A similar situation is encountered in Eq. (17). The cancellation occurs between two terms in the second square bracket when the value of α_2 is small. However, when accurate values of $L_\mu^\sigma(p,\alpha)$ are provided at the start, good accuracy is retained for all reasonable values of α_1, if only α_2 is moderate or large. Of course, instabilities become increasingly severe for higher values of μ, p_2, and σ. Similar to the previous case, the value of α_2 needs to be large enough to make Eq. (17) useful. Above $\alpha_2 = 3$ the instabilities are not severe for all μ, p_1, p_2, and σ needed in practice. In such case, Eq. (17) provides a reasonable way to build the necessary $w_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$, if only sufficiently accurate values of $L_\mu^\sigma(p,\alpha)$ are available. For smaller values of α_2 a different method is required.

Other quantities entering Eq. (3) do not pose significant numerical difficulties during evaluation by using closed-form expressions. Similarly, rather a minor loss of digits is observed during summation of the Neumann expansion or postprocessing of the resulting integrals. Therefore, instabilities connected with Eqs. (12) and (17) are the main obstacles to accurate calculation of two-center, two-electron exchange integrals over STOs by using the ellipsoidal expansion.

IV. CALCULATION OF THE $L_\mu^\sigma(p,\alpha)$ FUNCTIONS

Before presenting the working formulas, let us recall two simple recursions which make it possible to simplify the problem considerably. Both of them were recognized in the early works [2,3] and result directly from the properties of the Legendre functions and the integral representation (7). They are as follows:

$$L_\mu^0(p+1,\alpha) = \frac{(\mu+1)L_{\mu+1}^0(p,\alpha) + \mu L_{\mu-1}^0(p,\alpha)}{2\mu+1}, \tag{18}$$

$$L_\mu^{\sigma+1}(p,\alpha) = \frac{L_{\mu+1}^\sigma(p,\alpha) - L_{\mu-1}^\sigma(p,\alpha)}{2\mu+1}. \tag{19}$$

The first of the above equations is completely stable when used as it stands, i.e., in the direction of increasing p. Conversely, it is very unstable when used to increase μ at the cost of p. The only disadvantage of this formula is that one has to build $L_\mu^0(0,\alpha)$ with much higher μ than normally needed in order to produce the required $L_\mu^0(p,\alpha)$ integrals up to a given $p_{\max}$.

Considering Eq. (19), it can be used to build the final integrals $L_\mu^\sigma(p,\alpha)$ starting from the integrals with $\sigma = 0$. Most importantly, this recursion is also numerically stable for all relevant values of α when used for this purpose. To sum up, Eqs. (18) and (19) allow us to build $L_\mu^\sigma(p,\alpha)$ integrals very accurately, if only sufficiently correct values of $L_\mu^0(0,\alpha)$ are provided. Obviously, since now we require very large values of μ ($\mu = 50$ is not an overestimation), Eq. (12) cannot be used for that purpose for small values of α.

Before passing further, let us introduce an abbreviation $L_\mu(\alpha) := L_\mu^0(0,\alpha)$ which allows us to make our equations more compact and transparent.

A. Recursive calculation of the $L_\mu(\alpha)$ functions

Let us first note that Eqs. (12) and (15) are not perfectly suitable for a numerical evaluation. Despite their apparent simplicity, they introduce a number of auxiliary quantities which require a separate calculation. The optimal strategy is to utilize a recursive formula that connects the values of $L_\mu^0(0,\alpha)$ with different μ, since all integrals up to a given $\mu_{\max}$ are used to evaluate a bunch of the two-electron integrals. The required formula was obtained by Harris [15]:

$$L_{\mu+1}(\alpha) - \frac{2\mu+1}{\alpha} L_\mu(\alpha) - L_{\mu-1}(\alpha) = -\frac{2\mu+1}{\mu(\mu+1)} \frac{e^{-\alpha}}{\alpha}. \tag{20}$$

Unfortunately, this formula is not free from the numerical instabilities. The upward recursion is hopelessly unstable and probably useless. The downward recursion is also unstable, but in a more gentle and subtle way. As observed by Harris, the instabilities in the downward recursion arise only from contamination of the initial values by a multiple of the solution to the complementary recurrence problem, i.e., formula (20), with the right-hand side neglected. Solutions of the complementary recurrence problem are $(-1)^\mu i_\mu(\alpha)$ and $(-1)^\mu k_\mu(\alpha)$, multiplied by an α-dependent factor. The latter solution vanishes quickly and does not contaminate the final values. Therefore, the former is responsible for the numerical instabilities. As a result, the following algorithm can be proposed (downward recursion with adjustment):

(1) start with the exact initial values of $L_{\mu_{\max}}(\alpha)$ and $L_{\mu_{\max-1}}(\alpha)$ and carry out the recursive process (20) downward until $\mu = 0$ is reached;

(2) calculate $i_\mu(\alpha)$ for μ up to $\mu_{\max}$;

(3) compute $L_0(\alpha)$ by using the formula (15) and find the weighted difference $F = \frac{L_0(\alpha) - \bar{L}_0(\alpha)}{i_0(\alpha)}$, where $\bar{L}_\mu(\alpha)$ denotes the results of the downward recurrence;

(4) perform the "adjustment": $L_\mu(\alpha) = \bar{L}_\mu(\alpha) + F \times (-1)^\mu i_\mu(\alpha)$.

In the last step of the algorithm the error resulting from the contamination is eliminated. This is, in fact, a special case of the back substitution known from the Olver algorithm [21,22]. There are two major difficulties connected with the above procedure. First, one requires accurate values of $L_{\mu_{\max}}(\alpha)$ and $L_{\mu_{\max-1}}(\alpha)$ to be provided at the start. Second, the downward recursion has to be restarted occasionally with "fresh" values of $L_\mu(\alpha)$, somewhere in the middle of the recursive process to keep the value of F reasonably small.

The second problem can be solved in a brute-force fashion. In our implementation the downward recursion is restarted after each ten steps. For instance, when $\mu_{\max} = 30$ is required, the restarts occur at $\mu = 20$ and $\mu = 10$.

A much more troublesome problem is the calculation of the initial values, $L_{\mu_{\max}}(\alpha)$ and $L_{\mu_{\max-1}}(\alpha)$, for a given $\mu_{\max}$. We believe that the idea of Harris was to calculate those values from the explicit expressions by using an extended arithmetic precision. However, this requires an arbitrary precision package to be available and can be very time consuming, especially when a large number of restarts is required. We propose a different approach, which is closely related to the methods of computation of the Boys function [23] in the Gaussian integral theories [24]. Namely, for all required μ we created lookup tables which contain the values of the function $L_\mu(\alpha)$ and its several derivatives with respect to α, calculated on a properly suited grid. The grid spans over the interval $\alpha \in [0,100]$ with the step 0.01. We tabulated the data for $L_\mu(\alpha)$ with $\mu = 10,20,\ldots,100$, which is sufficient for practical purposes. Once the described lookup tables are created, the calculation of $L_\mu(\alpha)$ goes as follows. At input, the desired value of α is provided. If this value hits exactly one of the grid points, then the final value of $L_\mu(\alpha)$ is immediately returned. If not, the closest grid point is found and the values of $L_\mu(\alpha)$ and its several derivatives at this point are read from the lookup tables. Then, the Taylor expansion around the chosen grid point is performed, which makes it possible to compute the value of $L_\mu(\alpha)$ for the desired α. An even better performance of this approach can be reached if an expansion in the Chebyshev polynomials [16] is used instead of the ordinary Taylor series. However, our tests showed that the gain is fairly minor for this specific problem.

It is obvious that the method based on the lookup tables is stable and inexpensive. However, two usual problems are connected with this approach. First, the Taylor expansion tends to break down once α is close to zero. Second, only finite lookup tables can be stored, so that calculations are supported only up to some large value of α. In the following sections, we present two methods which are perfectly suitable for calculations of $L_\mu(\alpha)$ in either small or large α regime.

B. The differential equation for the $L_\mu(\alpha)$ functions

In this section we present a different approach to calculation of the $L_\mu^\sigma(p,\alpha)$ functions. Most of the working formulas available in the literature were derived starting from the integral representation, Eq. (7). We propose another line of attack, to derive a differential equation with respect to α which is obeyed by these integrals. The obtained differential equation is then solved by using properly tailored series expansions, substituting available analytical expressions in the regions where they lose numerical stability.

The derivation of the differential equation for $L_\mu(\alpha)$ starts with the well-known expression

$$(1-\xi^2)Q''_\mu(\xi) - 2\xi\, Q'_\mu(\xi) + \mu(\mu+1)Q_\mu(\xi) = 0, \quad (21)$$

where Q_μ are the Legendre functions of the second kind. By multiplying the above expression by $e^{-\alpha\xi}$ and integrating over ξ on the interval $[1,+\infty]$ one obtains

$$\begin{aligned} 0 = &\int_1^\infty Q''_\mu(\xi)e^{-\alpha\xi} - \int_1^\infty Q''_\mu(\xi)\xi^2 e^{-\alpha\xi} \\ &- 2\int_1^\infty Q'_\mu(\xi)\xi e^{-\alpha\xi} + \mu(\mu+1)\int_1^\infty Q_\mu(\xi)e^{-\alpha\xi}. \end{aligned} \quad (22)$$

The first two integrals need now to be integrated by parts twice in order to get rid of the derivatives of the Legendre functions. The results are

$$\begin{aligned} \int_1^\infty Q''_\mu(\xi)e^{-\alpha\xi} =& -e^{-\alpha}\lim_{\xi\to 1^+}[Q'_\mu(\xi)+\alpha Q_\mu(\xi)] \\ &+\alpha^2 L_\mu(\alpha), \\ \int_1^\infty Q''_\mu(\xi)\xi^2 e^{-\alpha\xi} =& -e^{-\alpha}\lim_{\xi\to 1^+}\xi^2[Q'_\mu(\xi)+\alpha Q_\mu(\xi)] \\ &-2\int_1^\infty Q'_\mu(\xi)\xi e^{-\alpha\xi} - 2\alpha L^0_\mu(1,\alpha) \\ &+\alpha^2 L^0_\mu(2,\alpha). \end{aligned} \quad (23)$$

By inserting the above expressions into the initial equation (21) we see that the third integral is canceled out. Additionally, it follows trivially from the definition that $L'_\mu(\alpha) := \frac{\partial}{\partial\alpha}L_\mu(\alpha) = -L^0_\mu(1,\alpha)$ and $L''_\mu(\alpha) := \frac{\partial^2}{\partial\alpha^2}L_\mu(\alpha) = L^0_\mu(2,\alpha)$. By making proper rearrangements one obtains readily

$$\begin{aligned} 0 = &e^{-\alpha}\lim_{\xi\to 1^+}(\xi^2-1)Q'_\mu(\xi) + \alpha\, e^{-\alpha}\lim_{\xi\to 1^+}(\xi^2-1)Q_\mu(\xi) \\ &-\alpha^2 L''_\mu(\alpha) - 2\alpha L'_\mu(\alpha) + [\mu(\mu+1)+\alpha^2]L_\mu(\alpha). \end{aligned} \quad (24)$$

To calculate the limits in the above expression, we have to recall the following series expansion of the Legendre functions of the second kind around the point $\xi = 1^+$:

$$\begin{aligned} Q_\mu(\xi) =& \tfrac{1}{2}\ln(2) - \tfrac{1}{2}\ln(\xi-1) - \gamma_E - \psi(\mu+1) \\ &+ \mathcal{O}(\xi-1), \end{aligned} \quad (25)$$

where $\psi(z)$ is the digamma function [16], so that the above limits evaluate to

$$\lim_{\xi\to 1^+}(\xi^2-1)Q'_\mu(\xi) = -1, \quad (26)$$

$$\lim_{\xi\to 1^+}(\xi^2-1)Q_\mu(\xi) = 0. \quad (27)$$

Therefore, the final form of the differential equation is disarmingly simple:

$$\alpha^2 L''_\mu(\alpha) + 2\alpha L'_\mu(\alpha) - [\mu(\mu+1)+\alpha^2]L_\mu(\alpha) = -e^{-\alpha}. \quad (28)$$

We believe that the differential equation (28) has not been known to the previous investigators. It is not obvious at first glance, however, if it can be used in practice. The next two sections of this paper are devoted to the derivation of the solutions of this differential equation which are applicable either in small or large α regimes. Especially the small α region is of primary importance since it is the regime where both the analytical expression, Eq. (12), and the recursive method, Eq. (20), fail to provide accurate results.

C. Calculation of the $L_\mu(\alpha)$ functions for small values of α

Considering the differential equation (28), it is trivial to conclude that the general solution can be written as

$$C^{(1)}_\mu i_\mu(\alpha) + C^{(2)}_\mu k_\mu(\alpha) + \mathcal{L}_\mu(\alpha), \quad (29)$$

where $i_\mu(\alpha) := i^0_\mu(0,\alpha)$ and $k_\mu(\alpha) := k^0_\mu(0,\alpha)$ are the solutions of the homogeneous problem, modified spherical Bessel functions. The constants $C^{(i)}_\mu$, $i = 1,2$, depend solely on μ and can be fixed thereafter by imposing proper initial conditions. The main problem lies then in the determination of the particular solution $\mathcal{L}_\mu(\alpha)$. Since in this section we are interested only in providing a new method applicable in the small α regime, our guess for the particular solution is

$$\mathcal{L}_\mu(\alpha) = \sum_{k=0}^{\infty} c^\mu_k \alpha^k + \ln(2\alpha)\sum_{k=\mu(+2)}^{\infty} d^\mu_k \alpha^k, \quad (30)$$

where the subscript $k = \mu(+2)$ denotes that the summation over k starts at μ and runs with the step of 2. In other words, we assume further that $d^\mu_{\mu+1}, d^\mu_{\mu+3}, \ldots$ are zero. The above formula is not intuitive and should, to some extent, be reasoned. The presence of the logarithmic terms is necessary by the virtue of the formula (12) (note the zero limit). The summation range in the second term is chosen *ad hoc* to give the simplest possible starting point that we are aware of. We could guess blindly that the second summation starts from zero and runs with the unit step. However, this shall make the derivation much more tedious without changing the final conclusion.

By inserting the above formula into the differential equation (28) and grouping the same powers of α together one obtains expression for the terms proportional to $\ln(2\alpha)$,

$$\sum_{k=\mu+2(+2)}^{\infty} \alpha^k\left[k(k+1)d^\mu_k - \mu(\mu+1)d^\mu_k - d^\mu_{k-2}\right] = 0, \quad (31)$$

which leads to a well-defined recursion relation,

$$d^\mu_k = \frac{d^\mu_{k-2}}{k(k+1)-\mu(\mu+1)}, \quad \text{for } k > \mu, \quad (32)$$

with d^μ_μ being arbitrary for a moment. Powers of α which are not multiplied by the logarithmic terms split naturally into two groups, giving rise to the second and the third expressions:

$$\sum_{k=2}^{\mu-1}\alpha^k\left[c^\mu_k k(k+1) - \mu(\mu+1)c^\mu_k - c^\mu_{k-2} + \frac{(-1)^k}{k!}\right] = 0, \quad (33)$$

$$\begin{aligned} \sum_{k=\mu}^{\infty}\alpha^k\Big[&c^\mu_k k(k+1) + d^\mu_k(2k+1) - \mu(\mu+1)c^\mu_k \\ &- c^\mu_{k-2} + \frac{(-1)^k}{k!}\Big] = 0. \end{aligned} \quad (34)$$

Additionally, one obtains two initial values of the coefficients $c_0^\mu = \frac{1}{\mu(\mu+1)}$ and $c_1^\mu = \frac{1}{2-\mu(\mu+1)}$ (from the indicial equation). Equations (33) and (34) can be solved to give the recursion relations

$$c_k^\mu k(k+1) - \mu(\mu+1)c_k^\mu - c_{k-2}^\mu + (-1)^k/k! = 0, \quad (35)$$

for $k \leqslant \mu - 1$, and

$$c_k^\mu k(k+1) + d_k^\mu(2k+1) - \mu(\mu+1)c_k^\mu - c_{k-2}^\mu + (-1)^k/k! = 0, \quad (36)$$

for $k \geqslant \mu + 1$. The value of d_μ^μ is fixed by the relation

$$d_\mu^\mu = \frac{c_{\mu-2}^\mu + (-1)^{\mu+1}/\mu!}{2\mu+1}. \quad (37)$$

Therefore, all coefficients appearing in the expression (30) are fixed by proper recursion relations apart from one remaining coefficient c_μ^μ, which can be fixed arbitrarily. The choice of this coefficient is purely conventional since it works in a tandem with the constants $C_\mu^{(i)}$, $i = 1,2$, from Eq. (29). For instance, one can put $C_\mu^{(1)}$ equal to zero and then fix the value of c_μ^μ from the initial conditions. Equivalently, c_μ^μ can be zeroed and the values of $C_\mu^{(i)}$ used to meet the initial conditions. Any intermediate choice is also acceptable. For simplicity and numerical convenience, we put $c_\mu^\mu = 0$ and transfer the responsibility for fulfilling the initial conditions to the coefficients $C_\mu^{(i)}$.

The equations presented here are rather simple, linear recursions which can be implemented efficiently. It is also easy to verify, even numerically, that no loss of digits is observed when these recursions are carried out. The only complication is that one can get lost in the order in which the recursions need to be performed. To address this problem, let us present a sketch of the algorithm that allows calculation of $\mathcal{L}_\mu(\alpha)$ for a given μ and α:

(1) calculate $c_0^\mu = \frac{1}{\mu(\mu+1)}$ and $c_1^\mu = \frac{1}{2-\mu(\mu+1)}$;
(2) build c_k^μ for $k \leqslant \mu - 1$ by using Eq. (35);
(3) calculate d_μ^μ from Eq. (37);
(4) build d_k^μ for $k \geqslant \mu + 2$ by using Eq. (32) up to a predefined value $k_{\max}$;
(5) set $c_\mu^\mu = 0$ (see text for the discussion);
(6) build c_k^μ for $k \geqslant \mu + 1$ by using Eq. (36) up to a predefined value $k_{\max}$;
(7) perform the final summations according to Eq. (30) and break them off at $k_{\max}$.

Alternatively, the values of c_k^μ or d_k^μ can be tabulated.

Having said this, the only remaining issue is the determination of the constants $C_\mu^{(i)}$, $i = 1,2$. The second coefficient can be fixed almost immediately from the following reasoning. The functions $L_\mu(\alpha)$ possess at most logarithmic singularities as α tends to zero. On the other hand, $k_\mu(\alpha)$ functions possess strong $1/\alpha^\mu$-type singularities in the limit of small α. Since $L_\mu(\alpha)$ cannot be contaminated by these kind of singularities, the constant $C_\mu^{(2)}$ must be fixed to zero for every μ. The remaining problem is to give an analytical expression for the constants $C_\mu^{(1)}$. The derivation flows without difficulties but it is rather tedious. Therefore, it has been moved to the Supplemental Material of this paper [25]. Obviously, it is easy to predict in advance how large values of μ are necessary in practice. Therefore, the values of $C_\mu^{(1)}$ can be included in a production program as a simple lookup table. This helps to minimize the cost of the corresponding calculations.

We have to note that an alternative approach to the calculation of $L_\mu^\sigma(p,\alpha)$ functions for small α exists. It was presented by Maslen and Trefry and significantly reformulated by Harris. Their working formula reads

$$L_\mu^\sigma(p,\alpha) = \sum_{k=0(+2)}^{p-\mu+\sigma-1} \frac{(-1)^\sigma(k+\mu-\sigma)!}{(k+2\mu+1)!!k!!} A_{p-\mu+\sigma-k-1}(\alpha) + (-1)^\mu i_\mu^\sigma(p,\alpha)E_1(\alpha) + e^{-\alpha}\sum_{t=0}^{\infty}\mathcal{M}_t^{\mu\sigma}(p)\alpha^t, \quad (38)$$

where

$$\mathcal{M}_t^{\mu\sigma}(p) = \sum_{j=0}^{(\mu+\sigma)/2}\sum_{l=0}^{t} \frac{(-1)^{l+j}(2\mu-2j-1)!!}{(\mu+\sigma-2j)!l!(t-l)!(2j)!!} \times T(2k_1+2\mu-2j+1, 2k_1+\mu-\sigma-p-l), \quad (39)$$

and $T(i,j)$ stands for the summation $\sum_{k=0}^\infty 1/(2k+i)(2k+j)$. The above expressions need to be strictly equivalent to the new method presented by us. Therefore, the only difference between the method of Harris and ours lies in the computational costs. The former requires calculations of the coefficients $\mathcal{M}_t^{\mu\sigma}(p)$ which are rather complicated, four-index quantities. Since it is not known in advance what is the biggest value of t required, it becomes risky to tabulate these coefficients. Production of the corresponding lookup table is cumbersome anyway. On the other hand, no recursive formulas that connect $\mathcal{M}_t^{\mu\sigma}(p)$ with different values of the parameters are known. Our method consists only of carrying out several simple linear recursions. Moreover, it is not necessary to evaluate any special functions such as E_1. To sum up, we found that our method is at least one order of magnitude faster for typical values of μ. Taking into consideration that both methods perform similarly when it comes to the accuracy, we recommend to use our method throughout.

To verify the validity of the new method we have benchmarked it against the results of calculations using the closed-form expressions. In order to obtain the reference values, we used the extended arithmetic precision provided by the *Mathematica* package. Results of the representative calculations are shown in Table I. We see that in the region $\alpha \leqslant 1$ our method behaves excellently. Additionally, one can verify that the closed-form formula, Eq. (12), fails to provide accurate values for small α. With our new method it is probably even possible to get accurate results for somewhat bigger values of α at the cost of including some extra terms in Eq. (30). However, above $\alpha = 1$ the recursive method (Sec. IV A) kicks in and it is favored in this regime.

Finally, let us mention that the equations presented here are also valid for $\mu = 0$. The main working equations (32) and (36) remain valid and generate no singularities, but become considerably simplified. For instance, recurrence relation (32) can now be explicitly solved to give $d_k = -1/(k+1)!$. To be consistent with the adopted convention, one has to put $c_0^0 = 0$

TABLE I. Exemplary calculations of the $L_\mu^0(0,\alpha)$ functions for some representative values of α. *Exact* denotes values calculated using Eq. (12) in extended arithmetic precision of 120 significant digits with the *Mathematica* package (all digits shown are correct). *Closed form* denotes calculations with Eq. (12) in the double precision arithmetic (around 15 significant figures). *New* column shows results of calculations with Eqs. (29) and (30), also in the double precision arithmetic. *Convergence* denotes a number of terms in Eq. (30) required to converge both summations to 15 significant digits. The symbol $[k]$ denotes the powers of 10, 10^k.

μ	Exact	Closed form	New	Convergence
		$\alpha = 0.1$		
0	2.08 622 255 552 379 [+00]	2.08 622 255 552 380 [+00]	2.08 622 255 552 379 [+00]	9
5	2.99 492 885 109 320 [−02]	2.99 496 650 695 801 [−02]	2.99 492 885 109 320 [−02]	9
10	8.21 061 998 897 917 [−03]	2.43 200 000 000 000 [+04]	8.21 061 998 897 917 [−03]	9
15	3.76 699 311 176 390 [−03]	3.41 288 409 261 670 [+16]	3.76 699 311 176 390 [−03]	9
20	2.15 334 499 798 711 [−03]	1.49 481 259 743 710 [+29]	2.15 334 499 798 711 [−03]	8
25	1.39 162 818 542 327 [−03]	2.43 369 948 821 855 [+42]	1.39 162 818 542 327 [−03]	8
30	9.72 733 864 877 070 [−04]	9.69 303 429 597 675 [+55]	9.72 733 864 877 070 [−04]	8
		$\alpha = 1.0$		
0	3.00 132 871 666 711 [−01]	3.00 132 871 666 711 [−01]	3.00 132 871 666 711 [−01]	20
5	1.15 009 425 728 751 [−02]	1.15 009 425 727 806 [−02]	1.15 009 425 728 751 [−02]	19
10	3.28 467 374 818 315 [−03]	3.28 468 531 370 163 [−03]	3.28 467 374 818 315 [−03]	19
15	1.52 016 466 579 821 [−03]	4.37 500 000 000 000 [+01]	1.52 016 466 579 821 [−03]	19
20	8.71 752 414 027 890 [−04]	4.82 344 960 000 000 [+07]	8.71 752 414 027 890 [−04]	18
25	5.64 232 304 101 147 [−04]	2.25 179 981 368 525 [+15]	5.64 232 304 101 147 [−04]	18
30	3.94 720 438 208 518 [−04]	3.92 900 891 374 755 [+24]	3.94 720 438 208 517 [−04]	18

and $c_1^0 = 1/2$. As an equivalent of Eq. (37) we have $d_0^0 = -1$ and Eq. (35) is of no use for $\mu = 0$. Additionally, to match the convention adopted in the Supplemental Material [25], as the solutions of the homogeneous differential equation one picks up $\sinh(\alpha)/\alpha$ and $\cosh(\alpha)/\alpha$. The latter solution can then be neglected due to strong singularity at the origin. As presented in Table I, numerical stability of the method for $\mu = 0$ is also very good.

D. Calculation of the $L_\mu(\alpha)$ functions for large values of α

Applications of the differential equation (28) are not limited to the small α expansion method presented in the previous section. As the next offspring of Eq. (28) we present the large α asymptotic expansion of the $L_\mu^0(\mu,\alpha)$ functions. As before, this expansion provides the starting values for the recursive relations (18) and (19). It is rather difficult to derive this expansion having only the integral representation (7) at hand.

One may ask, what is the point of deriving the large α asymptotic expansion of $L_\mu^0(\mu,\alpha)$ whereas the analytical formula (12) is perfectly stable in this regime? Indeed, the larger the value of α, the more numerically stable Eq. (12) becomes. Therefore, it seems to be an unnecessary redundancy to introduce an additional formula devoted specifically to the large α regime. This redundancy is only apparent, though. As one shall see shortly, the final asymptotic formula is very simple. It can be implemented highly efficiently and the calculation times are superior to the code based on Eq. (12).

In analogy with the previous section, the general solution of the differential equation (28) is given by the expression

$$D_\mu^{(1)} i_\mu(\alpha) + D_\mu^{(2)} k_\mu(\alpha) + \mathcal{L}_\mu^\infty(\alpha), \tag{40}$$

where $D_\mu^{(1)}$ and $D_\mu^{(2)}$ are new constants which we fix thereafter by using the initial conditions, and $\mathcal{L}_\mu^\infty(\alpha)$ is a particular solution. Since we are now interested in the large α regime, the latter takes the form

$$\mathcal{L}_\mu^\infty(\alpha) = e^{-\alpha} \sum_{k=1}^{\infty} \frac{a_k^\mu}{\alpha^k} + e^{-\alpha} \ln(2\alpha) \sum_{k=1}^{\infty} \frac{b_k^\mu}{\alpha^k}. \tag{41}$$

Derivation of the recursion formulas obeyed by the coefficients a_k^μ and b_k^μ is done in the standard fashion. The actual derivation is rather tedious and technical, so that we present only the final formulas,

$$b_{k+1}^\mu = b_k^\mu \frac{\mu(\mu+1) - k(k-1)}{2k}, \tag{42}$$

$$a_{k+1}^\mu = \frac{b_k^\mu (2k-1) + 2b_{k+1}^\mu - [k(k-1) - \mu(\mu+1)]\, a_k^\mu}{2k}, \tag{43}$$

for $k \geqslant 1$, with an additional requirement $b_1^\mu = 1/2$. The value of a_1^μ remains arbitrary and we can make a conventional choice, analogous to the choice $c_\mu^\mu = 0$ in the previous section. Therefore, we put $a_1^\mu = 0$ and then adjust properly the values of $D_\mu^{(1)}$ and $D_\mu^{(2)}$, so that the initial conditions are automatically met. A closer look at Eq. (42) reveals that b_k^μ with $k \geqslant \mu + 2$ are zero. In other words, the the second summation in Eq. (41) actually breaks off after $\mu + 1$ terms. Despite that, the first summation remains infinite. The quenching of the coefficients b_k^μ leads to simplifications in the formulas for a_k^μ. One has

$$a_{\mu+2}^\mu = b_{\mu+1}^\mu \frac{2\mu+1}{2\mu+2} \tag{44}$$

and

$$a_{k+1}^\mu = a_k^\mu \frac{\mu(\mu+1) - k(k-1)}{2k}, \tag{45}$$

for $k \geqslant \mu + 2$. In practice, the coefficients a_k^μ and b_k^μ are optimally either tabulated or computed on the fly by using the

TABLE II. Exemplary calculations of the $L_\mu^0(0,\alpha)$ functions for some representative values of α. *Exact* denotes values calculated using Eq. (12) in extended arithmetic precision of 32 significant digits with the *Mathematica* package (all digits shown are correct). *Asymptotic expansion* column shows results of calculations with Eqs. (40) and (41) in the double precision arithmetic. *Convergence* denotes a number of terms in Eq. (41) required to converge the summation to 15 significant digits. The symbol $[k]$ denotes the powers of 10, 10^k.

μ	Exact	Asymptotic expansion	Convergence
		$\alpha = 100.0$	
5	3.14 843 080 402 671 [−46]	3.14 843 080 402 670 [−46]	10
10	1.61 980 042 035 663 [−46]	1.61 980 042 035 663 [−46]	12
15	9.77 378 855 083 714 [−47]	9.77 378 855 083 711 [−47]	15
20	6.46 965 882 608 025 [−47]	6.46 965 882 608 030 [−47]	19
25	4.56 383 003 051 265 [−47]	4.56 383 003 051 411 [−47]	22
30	3.37 452 175 547 398 [−47]	3.37 452 175 547 026 [−47]	25
		$\alpha = 120.0$	
5	5.84 818 167 259 162 [−55]	5.84 818 167 259 162 [−55]	8
10	3.09 500 781 737 830 [−55]	3.09 500 781 737 831 [−55]	10
15	1.90 353 466 351 593 [−55]	1.90 353 466 351 592 [−55]	13
20	1.27 691 236 663 178 [−56]	1.27 691 236 663 178 [−56]	16
25	9.09 344 953 889 173 [−56]	9.09 344 953 889 132 [−56]	19
30	6.77 029 861 923 809 [−56]	6.77 029 861 923 817 [−56]	22

following algorithm:

(1) set $a_1^\mu = 0$ and $b_1^\mu = 1/2$;
(2) build coefficients b_k^μ for $k \leqslant \mu + 1$ by using Eq. (42);
(3) build coefficients a_k^μ for $k \leqslant \mu + 1$ by using Eq. (43);
(4) calculate $a_{\mu+2}^\mu$ from Eq. (44);
(5) build the remaining coefficients a_k^μ up to a predefined value $k_{\max}$ by using Eq. (45);
(6) perform the final summations according to Eq. (41) and break off the first summation at $k_{\max}$.

The last issue is to determine the values of the constants $D_\mu^{(1)}$ and $D_\mu^{(2)}$. The reasoning for fixing the first coefficient follows the same line as in the previous section. One sees from the integral representation (7) that $L_\mu(\alpha)$ vanishes as α tends to infinity because the integrand in Eq. (7) dies off at the exponential rate. On the other hand, the function $i_\mu(\alpha)$ diverges as α tends to infinity. Therefore, the constant $D_\mu^{(1)}$ must be equal to zero for every μ. It is more difficult to fix the value of the second constant, $D_\mu^{(2)}$. As before, the corresponding derivation is included in the Supplemental Material [25]. In Table II we present exemplary results of the calculations with the asymptotic expansion method.

Let us now summarize the advances reported in the present section. The most important result is the differential equation for the $L_\mu(\alpha)$ functions, Eq. (28). It has allowed us to derive both small and large α expansions of $L_\mu(\alpha)$. We proposed a practical realization of the recursive formula put forward by Harris. These three methods combined provide a new way to calculate $L_\mu(\alpha)$ for all required values of the parameters. Finally, recurrence relations (18) and (19) make it possible to build the final integrals $L_\mu^\sigma(p,\alpha)$ in a numerically stable fashion. Therefore, we can conclude that the problem of accurate and robust calculation of the $L_\mu^\sigma(p,\alpha)$ functions has been solved.

V. CALCULATION OF THE $W_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$ FUNCTIONS

Before presenting our results, let us give a brief summary of the methods available in the literature for the computation of the $W_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$ functions. In the early attempts, these integrals resisted to a direct integration and thus other schemes were proposed. Historically, the first fully analytical method was published by Kotani [6], who established a family of simple recursion relations. Roughly speaking, the major step of the Kotani recursions consists of building the integrals with larger values of μ, starting only with integrals with nonzero p_1, p_2, but $\mu = 0$. The values of the integrals $W_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$ grow very fast with the increasing p_1, p_2 but remain approximately constant (or decrease) when the value of μ is enlarged. Therefore, growing the value of μ at the cost of p_1 and p_2 is inherently connected with cancellation of huge numbers to a relatively small result. This is the reason for a dramatic loss of digits observed when the recursive process of Kotani is carried out up to large values of μ. We can roughly estimate that for the present purposes, the Kotani scheme can only be used if the values of α_1 and α_2 are both very large, of the order of 10–15. This is clearly highly unsatisfactory.

As mentioned in the Introduction, Maslen and Trefry [13] derived analytical expressions for the $W_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$ functions, which is undoubtedly a large step forward. However, these authors failed to recognize some of the numerical instabilities connected with their expressions. The main working formula of Maslen and Trefry, Eq. (17), cannot be used in practice for small values of α_2. Examples showing the failure of this expression are presented further in the paper. Therefore, the formulation of Maslen and Trefry alone cannot support large-scale calculations, especially when high angular momentum functions are present in the basis set.

An alternative approach is based on a set of new recursive formulas proposed by Fernández Rico *et al.* [14]. In this scheme a set of auxiliary quantities is introduced and the so-called "bisection" algorithm is used to carry out the recursion in two dimensions, where the diagonal elements correspond to the (scaled) $W_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$ functions. This recursive scheme is sufficient for small quantum numbers, but becomes progressively less stable when quantum numbers are high, especially when the nonlinear coefficients α_1, α_2

differ dramatically. Nonetheless, this scheme is elegant and straightforward and has a potential of being robust, which makes it suitable for small quantum numbers.

An important advance in the field is the 2002 work of Harris [15]. Harris recognized the problems connected with the equations of Maslen and Trefry and proposed new schemes for the computation of the $W_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$ functions. Small α_2 expansion of these integrals was considered but the working formula is not particularly useful, mainly due to convergence problems and the necessity to calculate the $L_\mu^\sigma(p,\alpha)$ functions with very large p. Another advance is the derivation of a new downward recursive scheme for the $W_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$ functions, completely disconnected from the method of Kotani. Unfortunately, the formulation of Harris is still not free of problems. It has strong connections with the method of Fernández Rico *et al.* [14] and suffers from similar difficulties. Additionally, restarts in the downward recursion need to be carried out often.

Before going further, let us recall an equation which appears in the recursive method of Kotani:

$$W_\mu^{\sigma+1}(p_1,p_2,\alpha_1,\alpha_2) = \frac{(\mu-\sigma)(\mu-\sigma+1)^2}{2\mu+1} W_{\mu+1}^\sigma(p_1,p_2,\alpha_1,\alpha_2) - (\mu-\sigma)(\mu+\sigma+1) \times W_\mu^\sigma(p_1+1,p_2+1,\alpha_1,\alpha_2) + \frac{(\mu+\sigma+1)(\mu+\sigma)^2}{2\mu+1} W_{\mu-1}^\sigma(p_1,p_2,\alpha_1,\alpha_2). \quad (46)$$

The above expression is sufficiently numerically stable for all relevant values of the parameters. Therefore, it provides an efficient and reliable method of generation of $W_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$ starting only with the integrals with $\sigma = 0$. Further in the article, we are concerned only with calculation of $W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$.

A. The differential equation for the $W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$ functions

In this section we derive a differential equation obeyed by the $W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$ functions. Derivations follow roughly the same idea as the one given in Sec. IV C, but are considerably more complicated. Fortunately, it also leads to an unexpectedly simple result. We introduce the abbreviation $W_\mu(p_1,p_2,\alpha_1,\alpha_2) := W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$.

Let us begin with the well-known differential equation for the Legendre functions:

$$\left(1-\xi_2^2\right)P_\mu''(\xi_2) - 2\xi_2 P_\mu'(\xi_2) + \mu(\mu+1)P_\mu(\xi_2) = 0. \quad (47)$$

By multiplying by $e^{-\alpha_2\xi_2}$ and integrating over the interval $[1,\xi_1]$ one arrives at

$$0 = \int_1^{\xi_1} P_\mu''(\xi_2)e^{-\alpha_2\xi_2} - \int_1^{\xi_1} \xi_2^2 P_\mu''(\xi_2)e^{-\alpha_2\xi_2} - 2\int_1^{\xi_1} \xi_2 P_\mu'(\xi_2)e^{-\alpha_2\xi_2} + \mu(\mu+1)\int_1^{\xi_1} P_\mu(\xi_2)e^{-\alpha_2\xi_2}. \quad (48)$$

The first and the second of the integrals need now to be integrated by parts twice. Noting that $P_\mu(\xi_2)$ is regular at $\xi_2 = 1$, one finds

$$\int_1^{\xi_1} P_\mu''(\xi_2)e^{-\alpha_2\xi_2} = e^{-\alpha_2\xi_1}[P_\mu'(\xi_1)+\alpha_2 P_\mu(\xi_1)] - e^{-\alpha_2}[P_\mu'(1)+\alpha_2 P_\mu(1)] + \alpha_2^2\int_1^{\xi_1} P_\mu(\xi_2)e^{-\alpha_2\xi_2} \quad (49)$$

and

$$\int_1^{\xi_1} \xi_2^2 P_\mu''(\xi_2)e^{-\alpha_2\xi_2} = -2\int_1^{\xi_1} \xi_2 P_\mu'(\xi_2)e^{-\alpha_2\xi_2}\xi_1^2 e^{-\alpha_2\xi_1}[P_\mu'(\xi_1)+\alpha_2 P_\mu(\xi_1)] - e^{-\alpha_2}[P_\mu'(1)+\alpha_2 P_\mu(1)] - 2\alpha_2\int_1^{\xi_1} \xi_2 P_\mu(\xi_2)e^{-\alpha_2\xi_2} + \alpha_2^2\int_1^{\xi_1} \xi_2^2 P_\mu(\xi_2)e^{-\alpha_2\xi_2}. \quad (50)$$

By inserting these identities into the initial equation many cancellations occur and finally we obtain

$$\left(1-\xi_1^2\right)P_\mu'(\xi_1)e^{-\alpha_2\xi_1} + \alpha_2\left(1-\xi_2^2\right)P_\mu(\xi_1)e^{-\alpha_2\xi_1} + 2\alpha_2\int_1^{\xi_1} \xi_2 P_\mu(\xi_2)e^{-\alpha_2\xi_2} - \alpha_2^2\int_1^{\xi_1} \xi_2^2 P_\mu(\xi_2)e^{-\alpha_2\xi_2} + \left[\mu(\mu+1)+\alpha_2^2\right]\int_1^{\xi_1} P_\mu(\xi_2)e^{-\alpha_2\xi_2} = 0. \quad (51)$$

The next step is to multiply both sides of the above equation by $Q_\mu(\xi_1)\xi_1^{p_1}e^{-\alpha_1\xi_1}$ and integrate by ξ_1 over the interval $[1,+\infty)$. Additionally, we make use of the identity

$$\left(1-\xi_1^2\right)P_\mu'(\xi_1) = \mu P_{\mu-1}(\xi_1) - \mu\xi_1 P_\mu(\xi_1) \quad (52)$$

to arrive at

$$\alpha_2^2\frac{\partial^2}{\partial\alpha_2^2}w_\mu(p_1,0,\alpha_1,\alpha_2) + 2\alpha_2\frac{\partial}{\partial\alpha_2}w_\mu(p_1,0,\alpha_1,\alpha_2) - \left[\mu(\mu+1)+\alpha_2^2\right]w_\mu(p_1,0,\alpha_1,\alpha_2) = +\mu\, T_{\mu-1,\mu}(p_1,\alpha_1+\alpha_2) - \mu\, T_{\mu\mu}(p_1+1,\alpha_1+\alpha_2) + \alpha_2 T_{\mu\mu}(p_1,\alpha_1+\alpha_2) - \alpha_2 T_{\mu\mu}(p_1+2,\alpha_1+\alpha_2). \quad (53)$$

where we have introduced, in analogy to Harris [15], a new function family $T_{\mu\nu}(p,\alpha)$,

$$T_{\mu\nu}(p,\alpha) = \int_1^\infty d\xi\, P_\mu(\xi)Q_\nu(\xi)\xi^p e^{-\alpha\xi}. \quad (54)$$

The above equation is a differential equation for $w_\mu(p_1,0,\alpha_1,\alpha_2)$ with respect to α_2. It has probably been unknown thus far. The remaining effort is to obtain the necessary series expansion valid in the small α_2 regime. Unfortunately, the above differential equation is not well suited for further developments because of the complicated form of the inhomogeneous term on the right-hand side. The resulting small α_2 expansion is complicated, slowly convergent and expensive to calculate. Additionally, the necessity to compute the $T_{\mu\nu}(p,\alpha)$ functions is a disadvantage. Therefore, we must seek a reformulation of some kind which allows a more convenient numerical evaluation.

The second part of the derivation starts with the observation that $w_\mu(0,p_1,\alpha_2,\alpha_1)$ can be cast in the following equivalent form:

$$w_\mu(0,p_1,\alpha_2,\alpha_1) = \int_1^\infty d\xi_2 P_\mu(\xi_2)\xi_2^{p_1} e^{-\alpha_1\xi_2} \int_{\xi_2}^\infty Q_\mu(\xi_1) e^{-\alpha_2\xi_1}. \quad (55)$$

Starting again with the differential equation (21), we multiply both sides by $e^{-\alpha_2\xi_1}$ and integrate over ξ_1 on the interval $[\xi_2,+\infty)$. The next step of the derivation is exactly the same as that used previously; the first two integrals are integrated by parts twice. The resulting expressions are inserted back into the initial equation. This procedure was described in detail earlier so here we list only the result:

$$\begin{aligned} &-\left(1-\xi_2^2\right)Q'_\mu(\xi_2)e^{-\alpha_2\xi_2} - \alpha_2\left(1-\xi_2^2\right)Q_\mu(\xi_2)e^{-\alpha_2\xi_2} \\ &+\alpha_2^2\int_{\xi_2}^\infty Q_\mu(\xi_1)e^{-\alpha_2\xi_1} + 2\alpha\int_{\xi_2}^\infty Q_\mu(\xi_1)\xi_1 e^{-\alpha_2\xi_1} \\ &-\alpha_2^2\int_{\xi_2}^\infty Q_\mu(\xi_1)\xi_1^2 e^{-\alpha_2\xi_1} = 0. \end{aligned} \quad (56)$$

Noting that exactly the same expression as (52) holds also for the Legendre functions of the second kind, Q_μ, we can get rid of the derivative in the first term of the above expression. Next, we multiply both sides by $P_\mu(\xi_2)\xi_2^{p_1}e^{-\alpha_1\xi_2}$ and integrate over ξ_2 on the interval $[1,+\infty)$. By invoking Eq. (55) one can bring the final result into the form

$$\begin{aligned} &\alpha_2^2\frac{\partial^2}{\partial\alpha_2^2}w_\mu(0,p_1,\alpha_2,\alpha_1) + 2\alpha_2\frac{\partial}{\partial\alpha_2}w_\mu(0,p_1,\alpha_2,\alpha_1) \\ &\quad -\left[\mu(\mu+1)+\alpha_2^2\right]w_\mu(0,p_1,\alpha_2,\alpha_1) \\ &= -\mu\, T_{\mu,\mu-1}(p_1,\alpha_1+\alpha_2) + \mu\, T_{\mu\mu}(p_1+1,\alpha_1+\alpha_2) \\ &\quad -\alpha_2 T_{\mu\mu}(p_1,\alpha_1+\alpha_2) + \alpha_2 T_{\mu\mu}(p_1+2,\alpha_1+\alpha_2), \end{aligned} \quad (57)$$

which constitutes the second required ingredient. Now, Eqs. (53) and (57) are added together, and by making use of Eq. (5) one finds

$$\begin{aligned} &\alpha_2^2\frac{\partial^2}{\partial\alpha_2^2}W_\mu(p_1,0,\alpha_1,\alpha_2) + 2\alpha_2\frac{\partial}{\partial\alpha_2}W_\mu(p_1,0,\alpha_1,\alpha_2) \\ &\quad -\left[\mu(\mu+1)+\alpha_2^2\right]W_\mu(p_1,0,\alpha_1,\alpha_2) \\ &= \mu\, T_{\mu-1,\mu}(p_1,\alpha_1+\alpha_2) - \mu\, T_{\mu,\mu-1}(p_1,\alpha_1+\alpha_2). \end{aligned} \quad (58)$$

To finally get rid of the $T_{\mu\nu}$ functions in the inhomogeneous term let us recall the transfer relation between the Legendre functions,

$$P_{\mu+1}(\xi)Q_\mu(\xi) - P_\mu(\xi)Q_{\mu+1}(\xi) = \frac{\Gamma(\mu+1)}{\Gamma(\mu+2)}, \quad (59)$$

which gives

$$\begin{aligned} &T_{\mu-1,\mu}(p_1,\alpha_1+\alpha_2) - T_{\mu,\mu-1}(p_1,\alpha_1+\alpha_2) \\ &\quad = -\frac{1}{\mu}A_{p_1}(\alpha_1+\alpha_2). \end{aligned} \quad (60)$$

By inserting this expression into the differential equation (57) one obtains the most important formula of this work,

$$\begin{aligned} &\alpha_2^2\frac{\partial^2}{\partial\alpha_2^2}W_\mu(p_1,0,\alpha_1,\alpha_2) + 2\alpha_2\frac{\partial}{\partial\alpha_2}W_\mu(p_1,0,\alpha_1,\alpha_2) \\ &\quad -\left[\mu(\mu+1)+\alpha_2^2\right]W_\mu(p_1,0,\alpha_1,\alpha_2) = -A_{p_1}(\alpha_1+\alpha_2). \end{aligned} \quad (61)$$

Noting that $W_\mu(p_1,0,\alpha_1,\alpha_2)$ is a complicated function of many variables, the simplicity of Eq. (61) is somehow surprising. First of all, we already know the solution of the homogeneous equation and it is the same as for the $L_\mu(\alpha)$ functions. The inhomogeneous term on the right-hand side is also a simple function which has a potential of providing reasonably uncomplicated expansions. In the next section we deal with the small α_2 expansion of $W_\mu(p_1,0,\alpha_1,\alpha_2)$, starting with the differential equation (61).

B. Calculation of the $W^0_\mu(p_1,p_2,\alpha_1,\alpha_2)$ functions for small values of α_2

Similar to what we did in Sec. IV C, the solution of the differential equation (61) can be written in the form

$$C^{(1)}_{\mu p_1}(\alpha_1)i_\mu(\alpha_2) + C^{(2)}_{\mu p_1}(\alpha_1)k_\mu(\alpha_2) + \mathcal{W}^{p_1}_\mu(\alpha_1,\alpha_2), \quad (62)$$

but the constants $C^{(1)}_{\mu p_1}(\alpha_1)$ and $C^{(2)}_{\mu p_1}(\alpha_1)$ are now dependent on the value of α_1; i.e., they are no longer discrete quantities. This leads to huge complications during their evaluation which shall be considered further. The function $\mathcal{W}^{p_1}_\mu(\alpha_1,\alpha_2)$ can be assumed to have the following series expansion in the small α_2 regime:

$$\mathcal{W}^{p_1}_\mu(\alpha_1,\alpha_2) = \sum_{k=0}^\infty c_k^{\mu p_1}\alpha_2^k + \ln(2\alpha_2)\sum_{k=\mu(+2)}^\infty d_k^{\mu p_1}\alpha_2^k. \quad (63)$$

Formally, one should set $c_k^{\mu p_1} := c_k^{\mu p_1}(\alpha_1)$ since the expansion coefficients are functions of α_1. However, this dependence is obvious and we decided to suppress it in order to make our equations more compact. The inhomogeneous term in Eq. (61) possesses the small α_2 expansion

$$-A_{p_1}(\alpha_1+\alpha_2) = \sum_{k=0}^\infty (-1)^{k+1}A_{p_1+k}(\alpha_1)\alpha_2^k. \quad (64)$$

To find the recursion relations for the coefficients $c_k^{\mu p_1}$ and $d_k^{\mu p_1}$, one has to insert the formula (63) into Eq. (61) and proceed in exactly the same way as in Sec. IV C. In fact, the only difference between these derivations lies in a small difference between the expansions of the inhomogeneous

terms. Therefore, there is no point in repeating this derivation here and we confine ourselves to the presentation of the final results. One first builds $c_k^{\mu p_1}$ coefficients up to, and including, $k = \mu - 1$ by using the formula

$$c_k^{\mu p_1}[k(k+1) - \mu(\mu+1)] - c_{k-2}^{\mu p_1} + (-1)^k A_{p_1+k}(\alpha_1) = 0, \tag{65}$$

with the initial values being $c_0^{\mu p_1} = A_{p_1}(\alpha_1)/\mu(\mu+1)$ and $c_1^{\mu p_1} = -\frac{-A_{p_1+1}(\alpha_1)}{2-\mu(\mu+1)}$. The first of the coefficients in the logarithmic part of the expansion is found from the relation

$$d_\mu^{\mu p_1}(2\mu+1) - c_{\mu-2}^{\mu p_1} + (-1)^\mu A_{p_1+\mu}(\alpha_1) = 0, \tag{66}$$

and then the other coefficients are calculated recursively as

$$d_k^{\mu p_1} = \frac{d_{k-2}^{\mu p_1}}{k(k+1) - \mu(\mu+1)}. \tag{67}$$

Finally, $c_k^{\mu p_1}$ coefficients with $k \geqslant \mu + 1$ are built from the formula

$$c_k^{\mu p_1}[k(k+1) - \mu(\mu+1)] + d_k^{\mu p_1}(2k+1) - c_{k-2}^{\mu p_1} + (-1)^k A_{p_1+k}(\alpha_1) = 0. \tag{68}$$

The choice of $c_\mu^{\mu p_1}$ is conventional and we can safely put it equal to zero, as discussed earlier. The remaining problem is the determination of the constants $C_{\mu p_1}^{(1)}(\alpha_1)$ and $C_{\mu p_1}^{(2)}(\alpha_1)$. Using a reasoning similar to one utilized previously, the value of $C_{\mu p_1}^{(2)}(\alpha_1)$ can immediately be fixed at zero. However, the derivation of an analytical formula for $C_{\mu p_1}^{(1)}(\alpha_1)$ is much more cumbersome and is presented in the Supplemental Material [25].

The small parameter expansions given here and in Sec. IV C seem to be completely analogous since the working formulas differ only by the presence of the A_k functions. There is, however, a big difference that practically limits the usefulness of the formula (63). The inhomogeneous term in the differential equation (28) has a small α Taylor expansion which is convergent for all relevant values of the parameter. Conversely, the series on the right-hand side of Eq. (64) has a finite radius of convergence. Namely, it is convergent if and only if the inequality $\alpha_2 < \alpha_1$ holds. From the mathematical point of view, when $\alpha_1 < \alpha_2$ one can make use of the symmetry relation

$$W_\mu(p_1,p_2,\alpha_1,\alpha_2) = W_\mu(p_2,p_1,\alpha_2,\alpha_1), \tag{69}$$

so that the roles of α_1 and α_2 are exchanged and the resulting series (64) falls within the convergence region. Unfortunately, the practical situation is more complex. It is understandable that when α_2 becomes close to α_1 the series (64) converges progressively slower. As a result, the series in Eq. (63) also suffers from the pathologically slow convergence pattern. This makes the presented method virtually useless unless α_1 and α_2 are reasonably spaced. Our numerical experience shows that the difference $|\alpha_1 - \alpha_2|$ must be larger than 2 to ensure a sufficiently fast rate of convergence.

Despite this shortcoming, the presented method solves a large majority of the problems connected with the small α_2 regime. Let us account for this statement by using the simplest possible example. For typical basis sets and reasonable values of the internuclear distances, only a handful of functions in the basis set can give rise to the values of α which fall in the problematic regime. Therefore, the number of integrals in which both α_1 and α_2 are small constitutes only a few percent, or even less, of the total number of integrals to be evaluated. On the other hand, the number of possible combinations in which α_2 is small but α_1 is large or moderate (or vice versa) is at least an order of magnitude larger. Typically, this situation corresponds to 10%–20% of the total number of integrals, which is definitely a significant fraction. The latter combination of α_2 and α_1 is perfectly suited for the present algorithm since in most cases the difference $|\alpha_1 - \alpha_2|$ is sufficiently large. Of course, the larger this difference is, the faster the series in Eq. (63) converge.

A slight inconvenience connected with Eq. (63) is that it includes explicitly only integrals with $p_2 = 0$. Higher values of p_2 have to be calculated by a consecutive differentiation with respect to α_2. Series present in Eq. (63) are trivial to differentiate analytically but the resulting series converge slightly slower. However, since the expansion coefficients $c_k^{\mu p_1}$ and $d_k^{\mu p_1}$ are shared between the integrals with different values of p_2 they have to be calculated only once. Therefore, the integrals with higher values of p_2 can be calculated at a small additional cost once a sufficiently large number of the expansion coefficients has been calculated in advance.

In Table III we present the calculated values of $W_\mu(p_1,p_2,\alpha_1,\alpha_2)$ for a selected set of α_1 and α_2. We included two the most challenging cases: when the difference between α_1 and α_2 is small and when this difference is larger but also the value of α_2 is larger. In both cases one could expect problems with convergence of the expansion or a loss of digits during the calculations. However, it turns out that for a reasonably wide range of μ, p_1, and p_2, our method provides an accuracy of at least 12–13 digits, and even more on the average. The number of terms needed to converge both summations in Eq. (63) is of the order of a few tens. This is acceptable, taking into consideration that the coefficients of the expansion are calculated efficiently by a fast and stable recursive process. Calculation of the constant $C_\mu^{(1)}(\alpha_1)$ (see Supplemental Material [25] for the accompanying discussion) consumes a significant fraction of the computational time. However, if a fast routine for the calculation of $L_\mu(p,\alpha)$ is provided, the overhead is still acceptable. To sum up, the series expansion method is superior to the analytical scheme which basically breaks down once the borderline of $\mu = 5$–10 has been crossed.

C. Calculation of the $W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$ functions for large values of α_2

The remaining formula which can straightforwardly be derived from the differential equation (61) is the asymptotic expansion of $W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$ for large values of α_2. This method is designed mainly to reduce costs of the calculations since the analytical expression, Eq. (17), is stable in this regime. However, as the values of α_i become large, one can expect integrals with comparable values of β_i. As mentioned earlier, in such cases the ellipsoidal expansion converges slower and quite large values of μ are required to achieve a desired accuracy. In this light, any method that significantly reduces the costs of the calculations for large α_i is definitely welcomed.

TABLE III. Exemplary calculations of the $W_\mu(p_1,p_2,\alpha_1,\alpha_2)$ functions for a few representative values of α_1 and α_2. *Exact* denotes values calculated using Eq. (17) in the extended arithmetic precision of 120 significant digits with the *Mathematica* package (all digits shown are correct). *Closed form* denotes calculations with Eq. (17) in the double precision arithmetic (around 15 significant figures). *New* column shows results of calculations with Eqs. (63) and (62), also in the double precision arithmetic. *Convergence* denotes a number of terms in Eq. (63) required to converge both summations to 15 significant digits. The symbol $[k]$ denotes the powers of 10, 10^k.

μ	Exact	Closed form	New	Convergence
		$\alpha_1 = 3.0, \alpha_2 = 0.5, p_1 = 0, p_2 = 0$		
0	1.04 486 860 277 951 [−02]	1.04 486 860 277 951 [−02]	1.04 486 860 277 951 [−02]	18
5	2.77 344 623 535 900 [−04]	2.77 344 591 894 414 [−04]	2.77 344 623 535 900 [−04]	20
10	7.76 549 171 325 524 [−05]	2.30 066 585 106 053 [+00]	7.76 549 171 325 524 [−05]	21
15	3.57 847 552 224 820 [−05]	1.28 381 137 541 490 [+12]	3.57 847 552 224 820 [−05]	22
20	2.04 886 403 945 215 [−05]	1.65 546 870 529 827 [+28]	2.04 886 403 945 215 [−05]	22
25	1.32 510 984 698 693 [−05]	1.05 032 000 000 000 [+44]	1.32 510 984 698 693 [−05]	23
		$\alpha_1 = 10.0, \alpha_2 = 2.0, p_1 = 0, p_2 = 0$		
0	3.06 472 238 344 757 [−07]	3.06 472 238 344 757 [−07]	3.06 472 238 344 757 [−07]	24
5	1.53 355 187 887 866 [−08]	1.53 355 187 883 772 [−08]	1.53 355 187 887 865 [−08]	27
10	4.50 949 894 593 816 [−09]	4.50 918 163 373 806 [−09]	4.50 949 894 593 816 [−09]	29
15	2.10 206 354 777 336 [−09]	2.30 624 503 190 029 [−05]	2.10 206 354 777 336 [−09]	29
20	1.20 875 103 359 696 [−09]	1.80 309 371 523 750 [+04]	1.20 875 103 359 697 [−09]	30
25	7.83 382 082 527 984 [−10]	1.00 728 429 616 952 [+14]	7.83 382 082 527 983 [−10]	30
		$\alpha_1 = 3.0, \alpha_2 = 0.5, p_1 = 5, p_2 = 0$		
0	7.48 701 970 608 968 [−02]	7.48 701 970 608 967 [−02]	7.48 701 970 608 968 [−02]	23
5	1.79 908 205 094 134 [−03]	1.79 908 423 520 203 [−03]	1.79 908 205 094 134 [−03]	26
10	5.03 737 212 031 091 [−04]	7.00 669 096 089 900 [+02]	5.03 737 212 031 091 [−04]	27
15	2.32 162 471 967 834 [−04]	5.29 745 051 970 872 [+15]	2.32 162 471 967 834 [−04]	27
20	1.32 933 530 186 838 [−04]	3.87 308 518 932 093 [+31]	1.32 933 530 186 838 [−04]	28
25	8.59 780 135 199 690 [−05]	1.22 261 970 344 498 [+47]	8.59 780 135 199 689 [−05]	28
		$\alpha_1 = 10.0, \alpha_2 = 2.0, p_1 = 5, p_2 = 0$		
0	5.18 010 434 002 219 [−07]	5.18 010 434 002 219 [−07]	5.18 010 434 002 218 [−07]	27
5	2.46 474 533 411 348 [−08]	2.46 474 533 415 337 [−08]	2.46 474 533 411 347 [−08]	30
10	7.21 451 958 797 078 [−09]	7.21 568 303 718 723 [−09]	7.21 451 958 797 074 [−09]	32
15	3.35 931 293 998 890 [−09]	1.15 756 754 553 331 [−04]	3.35 931 293 998 888 [−09]	33
20	1.93 091 293 856 568 [−09]	1.52 583 622 236 550 [+05]	1.93 091 293 856 568 [−09]	33
25	1.25 116 286 073 580 [−09]	1.49 697 488 157 192 [+16]	1.25 116 286 073 579 [−09]	34
		$\alpha_1 = 3.0, \alpha_2 = 0.5, p_1 = 0, p_2 = 5$		
0	1.28 329 165 081 863 [+01]	1.28 329 165 081 863 [+01]	1.28 329 165 081 863 [+01]	29
5	3.31 860 127 430 244 [−03]	3.30 708 670 298 918 [−03]	3.31 860 127 430 243 [−03]	29
10	5.87 022 662 870 030 [−04]	1.06 012 946 964 569 [+07]	5.87 022 662 870 029 [−04]	31
15	2.48 544 920 341 368 [−04]	5.63 197 344 090 803 [+20]	2.48 544 920 341 368 [−04]	32
20	1.38 157 704 830 518 [−04]	1.20 667 417 809 212 [+35]	1.38 157 704 830 518 [−04]	32
25	8.81 350 672 621 061 [−04]	6.40 686 820 917 187 [+51]	8.81 350 672 621 062 [−05]	33
		$\alpha_1 = 10.0, \alpha_2 = 2.0, p_1 = 0, p_2 = 5$		
0	3.58 469 358 658 655 [−06]	3.58 469 358 658 655 [−06]	3.58 469 358 658 655 [−06]	33
5	3.25 647 646 961 604 [−08]	3.25 647 645 628 771 [−08]	3.25 647 646 961 624 [−08]	33
10	7.83 161 224 394 686 [−09]	1.21 883 116 932 509 [−08]	7.83 161 224 394 619 [−09]	35
15	3.48 945 279 149 928 [−09]	6.77 701 483 960 846 [−01]	3.48 945 279 149 931 [−09]	38
20	1.97 344 359 497 490 [−09]	9.75 387 030 280 981 [+08]	1.97 344 359 497 492 [−09]	38
25	1.26 892 528 802 273 [−09]	2.09 712 604 451 529 [+19]	1.26 892 528 802 274 [−09]	39
		$\alpha_1 = 3.0, \alpha_2 = 0.5, p_1 = 5, p_2 = 5$		
0	1.16 382 213 456 748 [+02]	1.16 382 213 456 748 [+02]	1.16 382 213 456 748 [+02]	35
5	1.85 882 259 866 799 [−01]	1.87 725 859 472 266 [−01]	1.85 882 259 866 784 [−01]	33
10	3.82 726 511 424 708 [−02]	9.29 543 672 424 714 [+09]	3.82 726 511 424 750 [−02]	35
15	1.64 898 677 239 583 [−02]	9.02 398 949 011 648 [+23]	1.64 898 677 239 591 [−02]	37
20	9.21 265 882 301 559 [−03]	7.84 436 191 383 490 [+39]	9.21 265 882 301 558 [−03]	37
25	5.88 975 925 491 820 [−03]	2.12 258 315 835 870 [+56]	5.88 975 925 491 821 [−03]	38

TABLE III. (*Continued.*)

μ	Exact	Closed form	New	Convergence
		$\alpha_1 = 10.0, \alpha_2 = 2.0, p_1 = 5, p_2 = 5$		
0	6.31 318 894 312 804 [−06]	6.31 318 894 312 804 [−06]	6.31 318 894 312 804 [−06]	37
5	6.58 645 047 384 616 [−08]	6.58 645 051 424 336 [−08]	6.58 645 047 384 616 [−08]	37
10	1.61 556 791 342 107 [−08]	3.12 085 735 032 497 [−08]	1.61 556 791 341 897 [−08]	38
15	7.22 199 212 246 876 [−09]	1.23 801 100 582 205 [+01]	7.22 199 212 246 509 [−09]	41
20	4.08 869 377 197 726 [−09]	3.81 270 930 437 817 [+10]	4.08 869 377 197 785 [−09]	43
25	2.63 027 491 413 946 [−09]	1.01 348 114 811 063 [+22]	2.63 027 491 413 945 [−09]	43

To start the derivation, we first require an expression that defines the asymptotic behavior of the inhomogeneity in Eq. (61). It has the form

$$A_{p_1}(\alpha_1+\alpha_2) = e^{-\alpha_1-\alpha_2}\sum_{k=0}^{\infty}\frac{(-1)^k}{\alpha_2^{k+1}}\mathcal{C}_{kp_1}(\alpha_1), \tag{70}$$

where the coefficients $\mathcal{C}_{kp_1}(\alpha_1)$ are simple polynomials in α_1:

$$\mathcal{C}_{kp_1}(\alpha_1) = \sum_{l=0}^{\min(k,p_1)}\frac{p_1}{(p_1-l)!}(-1)^l\alpha_1^{k-l}\binom{k}{l}. \tag{71}$$

We did not manage to further simplify the above expression. However, it is clear that the coefficients $\mathcal{C}_{kp_1}(\alpha_1)$ are independent of μ and p_2 and therefore they need to be calculated only once for a given set of the $W^0_\mu(p_1,p_2,\alpha_1,\alpha_2)$ integrals.

Our ansatz for the large α_2 asymptotic solution of the differential equation (61) is

$$D^{(1)}_\mu(\alpha_1)i_\mu(\alpha_2) + D^{(2)}_\mu(\alpha_1)k_\mu(\alpha_2) + \mathcal{W}^{p_1,\infty}_\mu(\alpha_1,\alpha_2), \tag{72}$$

where the particular solution $\mathcal{W}^{p_1,\infty}_\mu$ is given by the inverse power expansion in α_2 multiplied by the proper exponential term:

$$\mathcal{W}^{p_1,\infty}_\mu(\alpha_1,\alpha_2) = e^{-\alpha_1-\alpha_2}\sum_{k=0}^{\infty}\frac{a_k^{\mu p_1}}{\alpha_2^{k+1}}. \tag{73}$$

In the above expression, $a_k^{\mu p_1}$ are implicitly assumed to be functions of α_1 and the corresponding notation was suppressed for brevity. The necessary recursive relation for $a_k^{\mu p_1}$ is found by inserting the above formula into the differential equation (61) and grouping the same inverse powers of α_2 together. Since the resulting coefficients must vanish identically, one obtains the following recursive relation:

$$a^\mu_{k+1} = \frac{(-1)^{k+1}\mathcal{C}_{kp_1}(\alpha_1) - [k(k+1)-\mu(\mu+1)]a^\mu_k}{2(k+1)}. \tag{74}$$

The first coefficient $a_0^{\mu p_1}$ remains arbitrary and must be fixed from the initial conditions. In the spirit of the previous approaches, we would put this coefficient equal to zero, and maneuver the values of the constants $D^{(1)}_\mu(\alpha_1)$ and $D^{(2)}_\mu(\alpha_1)$ in order to meet the initial conditions. However, because of the striking simplicity of the formula (73), it becomes attractive to set *both* of the constants equal to zero and then use $a_0^{\mu p_1}$ to meet the initial conditions. The derivation of the analytical formula for $a_0^{\mu p_1}$ is presented in the Supplemental Material [25].

We have to stress that the presented asymptotic expansion of $W^0_\mu(p_1,p_2,\alpha_1,\alpha_2)$ is valid only when α_2 is large and when $\alpha_2 > \alpha_1$. This happens because of the properties of the adopted series expansion of the inhomogeneous term, Eqs. (70) and (71). Additionally, to assert a rapid convergence of the series (73), the values of α_1 and α_2 need to be largely spaced. Simple numerical tests showed that the difference around 20 is a safe minimum, at least for small or moderate values of α_1. Of course, the larger the difference is, the faster the series (73) converges.

The above requirements may be considered to be a huge limitation of the presented procedure. However, let us note that the exchange integrals with both α_1 and α_2 large tend to be very small. As a result, they would be probably neglected by the Schwarz inequality or a similar screening method. Therefore, a majority of the non-negligible integrals with very large α_2 has a significantly lower value of α_1 (or vice versa), so that they fall into the regime where the asymptotic method is well suited.

In Table IV we present results of the calculations with our asymptotic method, compared with the "exact" values calculated from the analytic expression in the extended precision arithmetic. The higher values of p_2 in the integrals are obtained by a consecutive differentiation of the final formula (73) with respect to α_2. This differentiation is elementary, since the coefficients $a_k^{\mu p_1}$ do not depend on α_2. It follows from Table IV that the results obtained with the asymptotic expansion are accurate, if only α_1 and α_2 are sufficiently spaced and α_2 is large [the roles of α_1 and α_2 can be interchanged due to the symmetry relation (69)]. The convergence is also rapid in this case and, at most, a few tens of terms suffice to achieve the desired threshold. These results confirm the validity of the proposed asymptotic expansion, Eq. (73).

D. Final remarks on the analytic methods of calculation of the $W^0_\mu(p_1,p_2,\alpha_1,\alpha_2)$ functions

After presenting the working formulas, let us briefly summarize the advances reported in this section. We have derived the differential equation for $W^0_\mu(p_1,p_2,\alpha_1,\alpha_2)$ functions with respect to the nonlinear parameter α_2. Upon this differential equation, two important new methods of calculations have been built. The first one is aimed at the small α_i regime, where the analytical expression, Eq. (17), is numerically unstable. The second method provides an efficient and reliable method to calculate $W^0_\mu(p_1,p_2,\alpha_1,\alpha_2)$ for the asymptotically large values of α_2 or α_1. Each of the methods of calculation has its own drawbacks and limitations, which have been stressed earlier. Therefore, we have to investigate how these methods can be combined in order to produce a general algorithm. We also

TABLE IV. Exemplary calculations of the $W^0_\mu(p_1,0,\alpha_1,\alpha_2)$ functions for a few representative values of α_1 and α_2. *Exact* denotes values calculated using Eq. (17) in the extended arithmetic precision of 32 significant digits with the *Mathematica* package (all digits shown are correct). The *Asymptotic expansion* column shows results of calculations with Eq. (73) in the double precision arithmetic. *Convergence* denotes a number of terms in Eq. (73) required to converge the summation to the maximal possible accuracy. The symbol $[k]$ denotes the powers of 10, 10^k.

μ	Exact	Asymptotic expansion	Convergence
	$\alpha_1 = 5.0, \alpha_2 = 18.0, p_1 = 0$		
0	1.55 752 619 710 528 [−12]	1.55 752 619 710 358 [−12]	25
5	1.20 597 911 134 310 [−13]	1.20 597 911 134 129 [−13]	27
10	3.78 964 912 679 376 [−14]	3.78 964 912 679 764 [−14]	29
15	1.79 942 552 611 878 [−14]	1.79 942 552 612 880 [−14]	31
20	1.04 235 547 483 236 [−14]	1.04 235 547 484 335 [−14]	33
25	6.77 982 765 501 726 [−15]	6.77 982 765 505 423 [−15]	35
	$\alpha_1 = 5.0, \alpha_2 = 18.0, p_1 = 5$		
0	3.98 698 547 222 427 [−12]	3.98 698 547 222 507 [−12]	27
5	1.78 103 428 717 980 [−13]	1.78 103 428 718 353 [−13]	29
10	5.05 716 132 622 295 [−14]	5.05 716 132 622 680 [−14]	31
15	2.33 281 860 879 113 [−14]	2.33 281 860 879 422 [−14]	33
20	1.33 579 360 806 489 [−14]	1.33 579 360 807 802 [−14]	34
25	8.63 919 442 650 389 [−15]	8.63 919 442 656 241 [−15]	37
	$\alpha_1 = 8.0, \alpha_2 = 25.0, p_1 = 0$		
0	3.14 843 080 402 671 [−46]	3.14 843 080 402 670 [−46]	10
5	3.14 843 080 402 671 [−46]	3.14 843 080 402 670 [−46]	10
10	1.61 980 042 035 663 [−46]	1.61 980 042 035 663 [−46]	12
15	9.77 378 855 083 714 [−47]	9.77 378 855 083 711 [−47]	15
20	6.46 965 882 608 025 [−47]	6.46 965 882 608 030 [−47]	19
25	4.56 383 003 051 265 [−47]	4.56 383 003 051 411 [−47]	22
	$\alpha_1 = 8.0, \alpha_2 = 25.0, p_1 = 5$		
0	3.14 843 080 402 671 [−46]	3.14 843 080 402 670 [−46]	10
5	3.14 843 080 402 671 [−46]	3.14 843 080 402 670 [−46]	10
10	1.61 980 042 035 663 [−46]	1.61 980 042 035 663 [−46]	12
15	9.77 378 855 083 714 [−47]	9.77 378 855 083 711 [−47]	15
20	6.46 965 882 608 025 [−47]	6.46 965 882 608 030 [−47]	19
25	4.56 383 003 051 265 [−47]	4.56 383 003 051 411 [−47]	22

need to carefully check if the available methods cover the whole area of interest.

Figure 1 presents the first quarter of the (α_1,α_2) plane which corresponds to all possible combinations of the physically relevant integrals. We divide this plane into several nonoverlapping regions in which different methods of computation can be used in a stable and efficient manner. Generally speaking, we introduce four numerical parameters—λ_1, δ_1, λ_2, and δ_2—which control switching between algorithms:

(i) when the difference $|\alpha_1 - \alpha_2|$ is larger than δ_1 and either α_1 or α_2 is smaller than λ_1, the small α expansion presented in Sec. V B is used;

(ii) when both α_1 and α_2 are larger than λ_2 and the difference $|\alpha_1 - \alpha_2|$ is larger than δ_2, the asymptotic formulas described in Sec. V C need to be used;

(iii) when both α_1 and α_2 are larger than λ_1 and the requirements of the asymptotic expansion are not met, the analytical expression (17) is used.

The separation described above is depicted graphically on Fig. 1. This is a direct result of the symmetry relation, Eq. (69). The actual values of the parameters λ_1, δ_1, λ_2, and δ_2 need to be chosen on the basis of the numerical experiments. Our current estimate for "the best" values is $\lambda_1 \approx 3$, $\lambda_2 \approx 25$, $\delta_1 \approx 2$, and $\delta_2 \approx 20$. This choice is purely "empirical" and we are rather conservative in this respect. These values might change after gaining more numerical experience and observing the performance of the production code. One can even imagine that these values can be modified slightly from one basis set to another to match their specific requirements. Nonetheless, we believe that the values suggested by us are close to optimal.

From this brief study of the introduced regions one slightly afflictive conclusion can be drawn. There exists a region which is not covered by any of the analytical methods presently available. All methods are either numerically unstable or just invalid in the region where both α_1 and α_2 are smaller than λ_1 and the difference $|\alpha_1 - \alpha_2|$ is smaller than δ_1. However, this region is very small compared to the initial vast area of "no-man's land" before our methods were introduced. Numerical tests show that for typical basis sets and reasonable values of the internuclear separation, at most a few percent of the integrals fall in the problematic regime. Practically, it means that this region can be treated using a more computationally expensive, and possibly purely numerical, method without a significant overhead. The next section of the paper is devoted

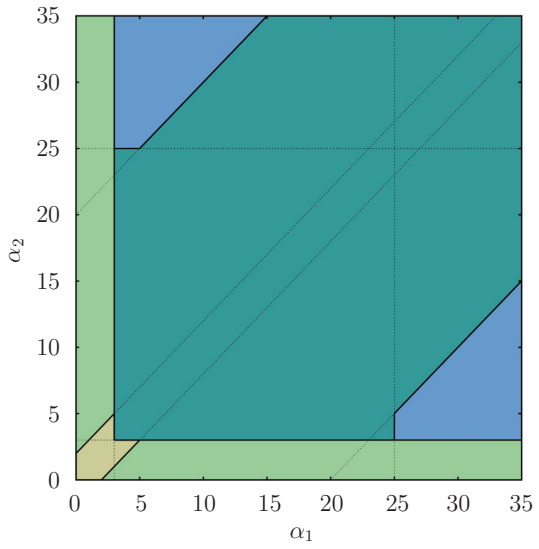

FIG. 1. (Color online) The (α_1,α_2) plane which corresponds to all possible combinations of the physically relevant integrals. The plane is divided into several regions in which different methods of computation of $W^0_\mu(p_1,p_2,\alpha_1,\alpha_2)$ are used. See Sec. V D for the discussion and comments.

entirely to the development of the "last resort" numerical integration scheme which completes the theory.

VI. THE "LAST RESORT" NUMERICAL INTEGRATION APPROACH

As mentioned above, to make the presented theory complete, we need a method which is reliable in the region where both α_1 and α_2 are smaller than λ_1 and the difference $|\alpha_1-\alpha_2|$ is smaller than δ_1. Since this region is tiny and a small number of integrals fall within it, a more expensive method can be used there. We propose to overcome this last obstacle by using a numerical integration. We consider it to be a temporary remedy, useful until a new analytical approach appears.

A direct numerical integration of Eq. (6) is rather daunting. Despite the apparent simplicity of the integrand, a two-dimensional quadrature rule has to be used. Such an approach has been pursued in the literature [26,27], but the resulting algorithms are typically very slow. We would like to adopt another line of attack. The inner integral in Eq. (17) is worked out analytically by using a general recursive process, and the outer one-dimensional integration is carried out numerically.

Let us first introduce a slightly more general integral class,

$$w^\sigma_{\mu\nu}(p_1,p_2,\alpha_1,\alpha_2)=\int_1^\infty d\xi_1\, Q^\sigma_\mu(\xi_1)\left(\xi_1^2-1\right)^{\sigma/2}\xi^{p_1}e^{-\alpha_1\xi_1}\times\int_1^{\xi_1}d\xi_2\, P^\sigma_\mu(\xi_2)\left(\xi_2^2-1\right)^{\sigma/2}\xi^{p_2}e^{-\alpha_2\xi_2} \tag{75}$$

and

$$W^\sigma_{\mu\nu}(p_1,p_2,\alpha_1,\alpha_2)=w^\sigma_{\mu\nu}(p_1,p_2,\alpha_1,\alpha_2)+w^\sigma_{\nu\mu}(p_2,p_1,\alpha_2\alpha_1), \tag{76}$$

so that integrals with $\mu=\nu$ correspond to the desired values and off-diagonal terms serve as auxiliary quantities. It becomes obvious that the values of p_1 and p_2 can easily be increased by means of the recurrence relation

$$W^\sigma_{\mu\nu}(p_1+1,p_2,\alpha_1,\alpha_2)=\frac{\mu+\sigma+1}{2\mu+1}W^\sigma_{\mu+1,\nu}(p_1,p_2,\alpha_1,\alpha_2)+\frac{\mu-\sigma}{2\mu+1}W^\sigma_{\mu-1,\nu}(p_1+1,p_2,\alpha_1,\alpha_2), \tag{77}$$

and from an analogous one for the parameter p_2. Note, that the above recursion is not self-starting, but initial values can be obtained by a procedure similar to that used by Harris [15], which is sufficiently numerically stable. When p_1 and p_2 are increased in this way, it remains to calculate the integrals with $p_1=p_2=0$. To proceed further we introduce the following function, which is, in substance, the inner integral in Eq. (75) at $p_2=0$:

$$\bar{k}^\sigma_\mu(x,\alpha)=\int_1^x d\xi\, P^\sigma_\mu(\xi)(\xi^2-1)^{\sigma/2}\,e^{-\alpha\xi}. \tag{78}$$

Note, that the above integrals obey the recursion relation (11). Herein, we shall use this recursion in a somehow different direction,

$$(2\mu+1)\bar{k}^{\sigma+1}_\mu(x,\alpha)+\bar{k}^\sigma_{\mu+1}(x,\alpha)=\bar{k}^\sigma_{\mu-1}(x,\alpha), \tag{79}$$

which can used to build all values with $\mu\leqslant\sigma$ starting with integrals with $\mu=\sigma$ and $\mu=\sigma-1$. To evaluate these starting values let us recall the following explicit expressions for the Legendre functions:

$$P^\mu_\mu(\xi)=\frac{(2\mu)!}{2^\mu\mu!}(\xi^2-1)^{\mu/2}, \tag{80}$$

$$P^{\mu-1}_\mu(\xi)=\frac{(2\mu)!}{2^\mu\mu!}\,\xi\,(\xi^2-1)^{\frac{\mu-1}{2}}. \tag{81}$$

Upon inserting the first of the above expressions in Eq. (78) and applying the binomial expansion to the term $(x+1)^\mu$ one arrives at

$$\bar{k}^\sigma_\mu(x,\alpha)=\frac{(2\mu)!}{2^\mu\mu!}\sum_{k=0}^{\mu}\binom{\mu}{k}\int_1^x d\xi\,(\xi-1)^\mu\xi^k\,e^{-\alpha\xi}. \tag{82}$$

Next, by applying the substitution $t=(\xi-1)/(x-1)$, expanding another term containing $t+1$ with the help of the binomial theorem, changing the order of summation, and writing the result in terms of the a_n function, Eq. (12) in Paper I, we find

$$\bar{k}^\mu_\mu(x,\alpha)=e^{-\alpha}\frac{(2\mu)!}{2^\mu\mu!}(x-1)^{\mu+1}\sum_{l=0}^{\mu}\binom{\mu}{l}\times(x-1)^l a_{\mu+l}\left[\alpha(x-1)\right]\sum_{k=l}^{\mu}\binom{\mu}{k}. \tag{83}$$

Note that an important feature of the above expression is that no loss of digits during computation is possible, all terms included in the double sum are positive and the functions a_n can be calculated with a strictly controlled precision by using the Miller algorithm [28]. The second quantity necessary to

initiate the recursive process, $\bar{k}_\mu^{\mu-1}(x,\alpha)$, is evaluated by using a very similar expression which can be derived starting with Eq. (81). Since the derivation follows exactly the same pattern with only minor differences, we do not present it here. Let us conclude that computation of $\bar{k}_\mu^\sigma(x,\alpha)$ from Eq. (83), its counterpart for $\sigma = \mu - 1$, and recursion relation (79) is free of any digital erosion and virtually guaranteed to give the machine precision in the result.

The final step of the method presented in this section is a numerical integration over the variable ξ_1. Thus, the integral $W_{\mu\nu}^\sigma(0,0,\alpha_1,\alpha_2)$ is approximated as a finite sum

$$W_{\mu\nu}^\sigma(0,0,\alpha_1,\alpha_2) \approx \sum_k w_k \left(x_k^2-1\right)^{\sigma/2}\left[Q_\mu^\sigma(x_k)e^{-\alpha_1 x_k}\bar{k}_\nu(x_k,\alpha_2) + Q_\nu^\sigma(x_k)e^{-\alpha_2 x_k}\bar{k}_\nu(x_k,\alpha_1)\right], \quad (84)$$

where x_k and w_k are the nodes and weights of a numerical integration rule. The other nonelementary quantities entering Eq. (84) are the scaled Legendre functions of the second kind, $Q_\mu^\sigma(x)(x^2-1)^{\sigma/2}$. Their evaluation has been discussed many times in the literature and it seems that they are best computed by downward recursion in μ followed by upward recursion in σ; see, for instance, Refs. [29–31]. Another troublesome aspect is choice of the numerical quadrature. The integrand, Eq. (84), is resistant to numerical integration and the conventional choice of the Gaussian-type quadratures requires a large number of nodes to match the prescribed accuracy requirements. There are two reasons for such a slow convergence with respect to the size of the quadrature. First, the integrand is sharply peaked around its maximum, especially for large μ/ν, and then vanishes very quickly (exponentially). Previous investigators also encountered this problem and proposed the so-called Möbius transformation [12], which makes the integrand more smooth and well behaved. This partial solution can be applied here straightforwardly. The second problem is the logarithmic singularity present in $Q_\mu(\xi)$ around $\xi = 1$. These singularities are, of course, integrable, but pose a considerable difficulty for the standard Gaussian quadratures with nonsingular weight functions. However, the so-called extended Gaussian quadratures are available which are designed to integrate functions of polynomial-logarithmic type and their performance is greatly improved compared to the standard schemes. Recently, accurate extended Gaussian quadratures with large numbers of nodes have been reported along with a general algorithm for computation of weights and abscissae (see Refs. [32–34] and references therein).

VII. CONCLUSIONS

In this paper, which constitutes the second part of the series, we considered the problem of efficient and accurate calculations of the two-center exchange integrals over STOs. The main advancement presented here is the derivation of the differential equations for two the most important basic quantities, the $L_\mu(p,\alpha)$ and $W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$ functions. The obtained differential equations are subsequently used to arrive at the series expansions for these basic functions. Series expansions for the small values of the parameters α_i are used to supplement the available analytic methods in situations where the digital erosion observed in the calculations becomes overwhelming. Asymptotic expansions for large values of α_i serve as a cheap alternative for the analytic expressions and are useful for further numerical or mathematical analysis. We have also considered numerical integration as an alternative in a small region where all analytic methods are not sufficiently accurate. All the available methods were combined in order to produce a general algorithm which allows an accurate calculation of the basic integrals within the whole region of practical interest.

Let us also note here that in the future much may be extended from the present work. The differential equation (61), due to its mathematical simplicity and compactness, offers an encouraging starting point for more advanced developments. Progress towards new expressions which remove the necessity to use the numerical integration is definitely welcomed. On the other hand, a completely different direction of the advancement can be pursued. An example could be the derivation of the large μ or σ expansions of the L and W functions. Since the large μ/σ expansions of the solutions to the homogeneous differential equation (61) are well-known, and the inhomogeneity does not depend on μ, such efforts might likely succeed.

The advances presented here and in the previous paper allow us to compute all molecular integrals required for the state-of-the-art *ab initio* calculations on the diatomic molecules with reasonable speed and sufficient accuracy. This allows us to launch an assault on the problem of bonding between two beryllium atoms. The third, and final, paper of the series is entirely devoted to the case study of the beryllium dimer.

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I. SUPPLEMENTAL MATERIAL FOR PAPER II

A. Analytical expression for $C_\mu^{(1)}$ constant in the small α expansion of $L_\mu^0(0,\alpha)$

The simplest way to find an analytical expression for $C_\mu^{(1)}$ is to compare our equations (29), (30) with the one proposed by Harris, Eqs. (38) and (39) (from Paper II). It is obvious that in the small α limit both expressions must lead to an exactly the same expansion. It is also possible to find $C_\mu^{(1)}$ by using only the formula (12) from Paper II but the derivation is much more tedious and too long for the purposes of this paper.

Let us begin by differentiating Eqs. (29), (30) μ times with respect to α. Next, by taking the limit $\alpha \to 0$ one obtains:

$$L_\mu^0(\mu,\alpha) = C_\mu^{(1)} \frac{(-1)^\mu \mu!}{(2\mu+1)!!} + (-1)^\mu d_\mu^\mu \log(2\alpha) + (-1)^\mu \mu! H_\mu d_\mu^\mu + \mathcal{O}(\alpha) \tag{1}$$

where the elementary identity $i_\mu^0(\mu,0) = \frac{\mu!}{(2\mu+1)!!}$ has been used. H_μ denotes the harmonic number (n-th harmonic number is the sum of the reciprocals of the first n natural numbers). In the above expression the convention $c_\mu^\mu = 0$ was used, according to the discussion presented in the main text. One the other hand, one can take the same limit in Eq. (38) from Paper II for $L_\mu^0(\mu,\alpha)$. Under these circumstances, the first term in Eq. (38) vanishes and one is left with:

$$L_\mu^0(\mu,\alpha) = -\gamma_E \frac{\mu!}{(2\mu+1)!!} - \frac{\mu!}{(2\mu+1)!!} \log(\alpha) + \mathcal{M}_0^{\mu 0}(\mu) + \mathcal{O}(\alpha). \tag{2}$$

In the derivation of the above expression the small α expansion of E_1 is useful: $E_1(\alpha) = -\gamma_E - \log(\alpha) + \mathcal{O}(\alpha)$. Expression for the coefficient $\mathcal{M}_0^{\mu 0}(\mu)$ becomes:

$$\mathcal{M}_0^{\mu 0}(\mu) = -\frac{\mu!}{(2\mu+1)!!} \log(2) + \widetilde{\mathcal{M}}_0^{\mu 0}(\mu), \tag{3}$$

with

$$\widetilde{\mathcal{M}}_0^{\mu 0}(\mu) = \sum_{j=0}^{\mu/2} \frac{(-1)^j (2\mu-2j-1)!!}{(\mu-2j)!(2j)!!(2\mu-2j+1)} \sum_{k=0}^{\mu-j} \frac{1}{2k+1}, \tag{4}$$

and it does not seem to simplify beyond that. Finally, we obtain the following expression:

$$L_\mu^0(\mu,\alpha) = -\gamma_E \frac{\mu!}{(2\mu+1)!!} - \frac{\mu!}{(2\mu+1)!!} \log(2\alpha) + \widetilde{\mathcal{M}}_0^{\mu 0}(\mu) + \mathcal{O}(\alpha). \tag{5}$$

Since the formulae (1) and (5) have to be identically the same, we can equate them. By comparing the quantities which are proportional to the logarithmic terms one obtains an equation for d_μ^μ:

$$-\frac{\mu!}{(2\mu+1)!!} = (-1)^\mu \mu! d_\mu^\mu, \tag{6}$$

and for the leftover

$$(-1)^\mu C_\mu^{(1)} \frac{\mu!}{(2\mu+1)!!} + (-1)^\mu \mu! H_\mu d_\mu^\mu = -\gamma_E + \widetilde{\mathcal{M}}_0^{\mu 0}(\mu). \tag{7}$$

By solving the first of the above equations for d_μ^μ and inserting the result back into the second equation one finally arrives at the desired analytical expression for $C_\mu^{(1)}$:

$$C_\mu^{(1)} = (-1)^\mu \left[H_\mu - \gamma_E + \frac{(2\mu+1)!!}{\mu!} \widetilde{\mathcal{M}}_0^{\mu 0}(\mu) \right]. \tag{8}$$

For practical use, the values of $C_\mu^{(1)}$ can simply be tabulated and included in the production program, as discussed in the main text.

B. Analytical expression for $D_\mu^{(2)}$ constant in the large α expansion of $L_\mu^0(0,\alpha)$

Starting with Eqs. (40) and (41) from Paper II, we multiply both sides by αe^α and take the limit of large α. Taking advantage of the asymptotic formula

$$k_\mu(\alpha) = e^{-\alpha}\left[\frac{1}{\alpha} + \mathcal{O}\left(\frac{1}{\alpha^2}\right)\right], \tag{9}$$

one finds that as $\alpha \to \infty$

$$\alpha e^\alpha L_\mu(\alpha) = D_\mu^{(2)} + \frac{1}{2}\log(2\alpha) + \mathcal{O}\left(\frac{1}{\alpha}\right), \tag{10}$$

since $b_1^\mu = 1/2$ and $a_1^\mu = 0$. Considering now Eq. (15) from Paper II and making use of the asymptotic formulae

$$A_p(\alpha) = e^{-\alpha}\left[\frac{1}{\alpha} + \mathcal{O}\left(\frac{1}{\alpha^2}\right)\right], \quad E_1(2\alpha) = e^{-2\alpha}\left[\frac{1}{2\alpha} + \mathcal{O}\left(\frac{1}{\alpha^2}\right)\right], \tag{11}$$

it becomes elementary to derive

$$\alpha e^\alpha L_0^0(p,\alpha) = \frac{1}{2}\left[\gamma_E + \log(2\alpha)\right] + \mathcal{O}\left(\frac{1}{\alpha}\right). \tag{12}$$

By inserting the above expression into Eq. (12) from Paper II and by using the asymptotic formula for A_p functions one arrives at

$$\alpha e^\alpha L_\mu(\alpha) = \frac{1}{2}\sum_s^\mu \mathcal{A}_s^{\mu 0}\left[\gamma_E + \log(2\alpha)\right] + \sum_s^{\mu-1}\mathcal{B}_s^{\mu 0}\cdot 1 + \mathcal{O}\left(\frac{1}{\alpha}\right). \tag{13}$$

It is rather simple to show that

$$\sum_s^\mu \mathcal{A}_s^{\mu 0} = 1, \quad \sum_s^{\mu-1}\mathcal{B}_s^{\mu 0} = -H_\mu, \tag{14}$$

and finally

$$\alpha e^\alpha L_\mu(\alpha) = \frac{1}{2}\left[\gamma_E + \log(2\alpha)\right] - H_\mu + \mathcal{O}\left(\frac{1}{\alpha}\right). \tag{15}$$

By comparing the above expression with the initial formula (10) we arrive at the desired expression $D_\mu^{(2)} = \frac{1}{2}\gamma_E - H_\mu$, which is trivial to calculate and completes the asymptotic theory presented in Subsection IV D of Paper II.

C. Analytical expression for the $C_\mu^{(1)}(\alpha_1)$ constant in the small α_2 expansion of $W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$

Let us begin with expressions (62) and (63) from Paper II. Let us differentiate these formulae μ times with respect to α_2. Since $C_{\mu p_1}^{(2)}(\alpha_1)$ and $a_\mu^{\mu p_1}$ have already been set to zero (see the main text for the discussion) one readily obtains the following expression in the limit $\alpha_2 \to 0^+$:

$$W_\mu(p_1,\mu,\alpha_1,\alpha_2) = (-1)^\mu \mu!\left[\frac{C_{\mu p_1}^{(1)}(\alpha_1)}{(2\mu+1)!!} + e^{-\alpha_1} H_\mu\, b_\mu^{\mu p_1} + e^{-\alpha_1}\, b_\mu^{\mu p_1}\log(2\alpha_2)\right] + \mathcal{O}(\alpha_2). \tag{16}$$

Let us now consider the limit $\alpha_2 \to 0^+$ in Eq. (5) from Paper II with $p_2 = \mu$ and $\sigma = 0$. The first term on the right hand side is regular at $\alpha_2 = 0$ but the second term needs to be rewritten in the following way:

$$w_\mu(\mu,p_1,\alpha_2,\alpha_1) = \int_1^\infty d\xi_1 Q_\mu(\xi_1)\xi_1^\mu e^{-\alpha_2\xi_1}\int_1^{\xi_1} d\xi_2 P_\mu(\xi_2)\xi_2^{p_1} e^{-\alpha_1\xi_2} = \int_1^\infty d\xi_1 Q_\mu(\xi_1)\xi_1^\mu e^{-\alpha_2\xi_1}\int_1^{\xi_1} d\xi_2 P_\mu(\xi_2)\xi_2^{p_1} e^{-\alpha_1\xi_2}$$
$$-\int_1^\infty d\xi_1 Q_\mu(\xi_1)\xi_1^\mu e^{-\alpha_2\xi_1}\int_{\xi_1}^\infty d\xi_2 P_\mu(\xi_2)\xi_2^{p_1} e^{-\alpha_1\xi_2} = k_\mu(p_1,\alpha_1)L_\mu(\mu,\alpha_2) - \bar{w}_\mu(\mu,p_1,\alpha_2,\alpha_1). \tag{17}$$

Note, that now the first term in the above expression contains the logarithmic singularity at $\alpha_2 = 0$ but the second term is regular. Additionally, we can now make use of Eq. (5) to obtain the small α_2 formula:

$$w_\mu(\mu, p_1, \alpha_2, \alpha_1) = k_\mu(p_1, \alpha_1) \left[-\gamma_E \frac{\mu!}{(2\mu+1)!!} - \frac{\mu!}{(2\mu+1)!!} \log(2\alpha_2) + \widetilde{\mathcal{M}}_0^{\mu 0}(\mu) \right] - \bar{w}_\mu(\mu, p_1, 0, \alpha_1) + \mathcal{O}(\alpha_2), \tag{18}$$

and returning to Eq. (5) from Paper II we finally have

$$\begin{aligned} W_\mu(p_1, \mu, \alpha_1, \alpha_2) = w_\mu(p_1, \mu, \alpha_1, 0) - \bar{w}_\mu(\mu, p_1, 0, \alpha_1) + k_\mu(p_1, \alpha_1) \times \\ \times \left[-\gamma_E \frac{\mu!}{(2\mu+1)!!} - \frac{\mu!}{(2\mu+1)!!} \log(2\alpha_2) + \widetilde{\mathcal{M}}_0^{\mu 0}(\mu) \right] + \mathcal{O}(\alpha_2), \end{aligned} \tag{19}$$

It is now possible to compare the expressions (16) and (19). Terms proportional to the logarithm give rise to the following equality

$$(-1)^\mu \mu! e^{-\alpha_1} b_\mu^{\mu p_1} = -\frac{\mu!}{(2\mu+1)!!} k_\mu(p_1, \alpha_1), \tag{20}$$

and the leftover

$$\begin{aligned} (-1)^\mu \mu! \left[\frac{C^{(1)}_{\mu p_1}(\alpha_1)}{(2\mu+1)!!} + e^{-\alpha_1} H_\mu \, b_\mu^{\mu p_1} \right] = w_\mu(p_1, \mu, \alpha_1, 0) - \bar{w}_\mu(\mu, p_1, 0, \alpha_1) \\ + k_\mu(p_1, \alpha_1) \left[-\gamma_E \frac{\mu!}{(2\mu+1)!!} + \widetilde{\mathcal{M}}_0^{\mu 0}(\mu) \right]. \end{aligned} \tag{21}$$

The first of the above expressions can be solved for $b_\mu^{\mu p_1}$ and the result is inserted in the second one. After some rearrangements the final result reads:

$$\frac{(-1)^\mu \mu!}{(2\mu+1)!!} C^{(1)}_{\mu p_1}(\alpha_1) = w_\mu(p_1, \mu, \alpha_1, 0) - \bar{w}_\mu(\mu, p_1, 0, \alpha_1) + k_\mu(p_1, \alpha_1) \left[(H_\mu - \gamma_E) \frac{\mu!}{(2\mu+1)!!} + \widetilde{\mathcal{M}}_0^{\mu 0}(\mu) \right]. \tag{22}$$

The above expression is of little use if there is no simple way to calculate the values of $w_\mu(p_1, \mu, \alpha_1, 0)$ and $\bar{w}_\mu(\mu, p_1, 0, \alpha_1)$. In the following we show that those two integrals can be simply expressed through the L_μ functions. The simplest way to obtain the integral $w_\mu(p_1, \mu, \alpha_1, 0)$ is to start with Eq. (54) from the 2002 paper of Harris [F. E. Harris, Int. J. Quantum Chem. **88**, 701 (2002)]. When $\alpha_2 = 0$ one obtains simply:

$$w_\mu(p_1, \mu, \alpha_1, 0) = \sum_s^\mu A_s^{\mu 0} \frac{1}{\mu + s + 1} L_\mu(p_1 + \mu + s + 1, \alpha_1) - L_\mu(p_1, \alpha_1) \bar{i}_\mu(\mu, 0), \tag{23}$$

where

$$\bar{i}_\mu(\mu, 0) = \int_0^1 d\xi P_\mu(\xi) \, \xi^\mu = \sum_s^\mu A_s^{\mu 0} \frac{1}{\mu + s + 1}. \tag{24}$$

Therefore, the explicit expression is

$$w_\mu(p_1, \mu, \alpha_1, 0) = \sum_s^\mu \frac{A_s^{\mu 0}}{\mu + s + 1} \Big[L_\mu(p_1 + \mu + s + 1, \alpha_1) - L_\mu(p_1, \alpha_1) \Big]. \tag{25}$$

To calculate the second required ingredient - analytical expression for $\bar{w}_\mu(\mu, p_1, 0, \alpha_1)$ one starts with the explicit expression

$$\bar{w}_\mu(\mu, p_1, 0, \alpha_1) = \int_1^\infty d\xi_1 \, Q_\mu(\xi_1) \, \xi_1^\mu \int_{\xi_1}^\infty d\xi_2 \, P_\mu(\xi_2) \, \xi_2^{p_1} \, e^{-\alpha_1 \xi_2} = \sum_s^\mu A_s^{\mu 0} \int_1^\infty d\xi_1 \, Q_\mu(\xi_1) \, \xi_1^\mu \int_{\xi_1}^\infty d\xi_2 \, \xi_2^{p_1 + s} \, e^{-\alpha_1 \xi_2}, \tag{26}$$

and by substitution of variables $t = \xi_2 / \xi_1$ in the inner integral one immediately recognises that it can be rewritten as

$$\bar{w}_\mu(\mu, p_1, 0, \alpha_1) = \sum_s^\mu A_s^{\mu 0} \int_1^\infty d\xi_1 \, Q_\mu(\xi_1) \, \xi_1^{\mu + p_1 + s + 1} A_{p_1 + s}(\alpha_1 \xi_1). \tag{27}$$

Finally, when Eq. (19) from Paper I is inserted one obtains

$$\bar{w}_\mu(\mu,p_1,0,\alpha_1)=\sum_s^\mu A_s^{\mu 0}\frac{(p_1+s)!}{\alpha_1^{p_1+s+1}}\sum_{k=0}^{p_1+s}\frac{\alpha_1^k}{k!}L_\mu(\mu+k,\alpha_1), \tag{28}$$

which formally completes the theory. Note, that Eq. (21) introduces some digital erosion but it is much better conditioned than the original expressions of Maslen and Trefry when α_1 is small.

D. Analytical expression for the $a_k^{\mu p_1}$ constant in the large α_2 expansion of $W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$

If one considers the asymptotic formula, Eq. (73) from Paper II, the following expression is elementary

$$\lim_{\alpha_2\to\infty} e^{\alpha_1+\alpha_2}\alpha_2 W_\mu^0(p_1,0,\alpha_1,\alpha_2)=\lim_{\alpha_2\to\infty} e^{\alpha_1+\alpha_2}\alpha_2 \mathcal{W}_\mu^{p_1,\infty}(\alpha_1,\alpha_2)=a_0^{\mu p_1}, \tag{29}$$

since both constants $D_\mu^{(1)}(\alpha_1)$ and $D_\mu^{(2)}(\alpha_1)$ are *a priori* set identically equal to zero for all values of the parameters. On the other hand, let us make use of the analytical expressions for $W_\mu^0(p_1,0,\alpha_1,\alpha_2)$, Eqs. (5) and (17) from Paper II. Let us first note, that among many terms present in this equation, only the term $L_\mu^0(p_1,\alpha_1)k_\mu^0(0,\alpha_2)$ contributes to the above limit. This fact can be deduced straightforwardly by using the asymptotic theory of the $L_\mu^0(p,\alpha)$ functions given earlier and Eq. (9). In other words, one can show that

$$\lim_{\alpha_2\to\infty} e^{\alpha_1+\alpha_2}\alpha_2\Big[W_\mu^0(p_1,0,\alpha_1,\alpha_2)-L_\mu^0(p_1,\alpha_1)k_\mu^0(0,\alpha_2)\Big]=0, \tag{30}$$

for every μ, p_1 and α_1. Therefore

$$\lim_{\alpha_2\to\infty} e^{\alpha_1+\alpha_2}\alpha_2 W_\mu^0(p_1,0,\alpha_1,\alpha_2)=e^{\alpha_1}L_\mu^0(p_1,\alpha_1)\lim_{\alpha_2\to\infty} e^{\alpha_2}\alpha_2 k_\mu^0(0,\alpha_2)=e^{\alpha_1}L_\mu^0(p_1,\alpha_1), \tag{31}$$

by the virtue of Eq. (9) and the final formula reads $a_0^{\mu p_1}=e^{\alpha_1}L_\mu^0(p_1,\alpha_1)$. As one can see, in the asymptotic theory of the $W_\mu^0(p_1,p_2,\alpha_1,\alpha_2)$ functions, the necessity to calculate $L_\mu^0(p_1,\alpha_1)$ integrals with arbitrary values of the parameters is indispensable.

Paper III

"Reexamination of the calculation of two-center, two-electron integrals over Slater-type orbitals. III. Case study of the beryllium dimer"

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Commentary

In Paper I and Paper II we claimed that the novel techniques developed for evaluation of the two-centre integrals over STOs are sufficient to support accurate *ab initio* calculations for diatomics in large basis sets. Such a claim must be backed by a practical example. This is the main goal of the third paper where accurate quantum-chemical study of the beryllium dimer is presented.

The first goal of the Paper III is to develop a systematic sequence of STOs basis sets which can be used in accurate molecular calculations. We provide numerous details concerning the optimisation of the exponents, construction of the basis sets satisfying the correlation consistency principle, and other practical problems. We also discuss similarities and differences in the optimisation procedures between the GTOs and STOs. Benchmark results for the beryllium atom are provided and extrapolation towards the complete basis set is discussed.

Since Paper III is mostly the proof of principle of the methods developed in the previous two articles, we performed calculations only for a single internuclear

separation corresponding to the minimum on the potential energy curve. This allows to determine the interaction energy of the beryllium dimer but not the binding energy, vibrational energy levels, etc. The latter issues are considered in Paper VII.

To evaluate accurate value of the interaction energy for the beryllium dimer it was divided into a set of physically meaningful contributions, e.g. four-electron valence, core-core and core-valence, relativistic and few others. Each contribution is evaluated at the best level of theory presently available with the largest feasible basis set. For example, valence effects are treated with the help of the full CI method in basis sets of double- to sextuple-zeta quality. Apart from standard Born-Oppenheimer contribution we calculate the relativistic contributions (which are found to be surprisingly large) and estimate the QED and adiabatic effect. The total interaction energy calculated in this work differs by only about 1 cm^{-1} from the most recent empirical value.

Finally, we summarise the most important advantages of STOs which contributed to the accuracy of the results. Some of them are due to the correct description of the nuclear cusp, e.g. accuracy of the relativistic corrections and core contributions. Other advantages are somewhat more unexpected, e.g. a good reliability of the extrapolations towards the complete basis. To sum up, we believe that the most important massage of Paper III is that STOs can now routinely be used in accurate *ab initio* calculations for diatomic systems.

Reexamination of the calculation of two-center, two-electron integrals over Slater-type orbitals. III. Case study of the beryllium dimer

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In this paper we present results of *ab initio* calculations for the beryllium dimer with a basis set of Slater-type orbitals (STOs). Nonrelativistic interaction energy of the system is determined using the frozen-core full configuration interaction calculations combined with high-level coupled-cluster correction for inner-shell effects. We have developed STO basis sets, ranging in quality from double to sextuple ζ, which are used in these computations. Principles of their construction are discussed and several atomic benchmarks are presented. Relativistic effects of order α^2 are calculated perturbatively by using the Breit-Pauli Hamiltonian and are found to be significant. We also estimate the leading-order QED effects. Influence of the adiabatic correction is found to be negligible. Finally, the electronic binding energy of the beryllium dimer is determined to be $929.0 \pm 1.9\,\mathrm{cm}^{-1}$, in a very good agreement with the recent experimental value.

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I. INTRODUCTION

State-of-the-art *ab initio* electronic structure calculations are very important for the new emerging field at the border of chemistry and physics: the studies of ultracold molecules. During the past decades, experimental advances in laser cooling and trapping of neutral atoms have opened a door for the formation of ultracold diatomic molecules by photoassociation [1] and magnetoassociation [2] techniques. In this respect, *ab initio* calculations of the potential energy curves and coupling matrix elements between the electronic states turned out to be crucial to interpret the experimental observations. See, for instance, Ref. [3] for the theoretical explanation of the unusual quadratic Zeeman shifts in the Sr_2 molecule, or Ref. [4] for interpretation of the observed subradiant states of Sr_2. Electronic structure calculations can also be used to predict new schemes for the formation of ultracold diatomic molecules [5–9]. Apart from that, state-of-the-art first-principles calculations are used in metrology, e.g., to determine the pressure standard [10]. Last, but not least, accurate interatomic interaction potentials are of significant importance in search for a new physics. See, e.g., Ref. [11] for a theoretical study of the QED retardation effect of the helium dimer and the work of Zelevinsky *et al.* [12] for a joint experimental-theoretical effort towards determination of the proton-electron mass ratio time variation. Additionally, one can mention the work of Schwerdtfeger *et al.* [13] on the Sr_2 molecule where time variation of the fine structure constant is investigated.

All the aforementioned physical applications require high-precision theoretical data. Slater-type orbitals (STOs) are expected to improve the description of many-electron systems, thus leading to results more accurate than available at present. In the first two papers of the series we proposed efficient algorithms for the calculation of two-center integrals over STOs [14,15]. As the first application of the STO integral code we performed calculations for the beryllium dimer in its ground $^1\Sigma_g^+$ state. This is a challenging system, from both the theoretical and the experimental points of view. From the theory side, it has already been known that in order to reach accurate results, very advanced quantum chemistry methods must be used. In fact, probably the first calculations performed for this system by Fraga and Ransil [16], using the restricted Hartree-Fock (RHF) method, led to the conclusion that the potential energy curve is purely repulsive. Further inclusion of the electron correlation, by using the configuration interaction (CI) method with single and double substitutions (CISD), appeared to confirm this observation [17]. However, more refined calculations with the same method indicated an existence of a weak bond [18,19], with the interaction energy of the order of several tens of cm^{-1} and equilibrium distance of $\approx$5 Å, which is characteristic for the van der Waals molecules such as Ne_2. A similar conclusion was found in a study [20] employing the coupled-cluster (CC) methods with double (and single) excitations (CCD, CCSD).

However, somehow later Harrison and Handy [21] performed frozen-core full configuration interaction (FCI) calculations and found that the interaction energy is at least several hundreds of cm^{-1} larger. Even more importantly, they reported the presence of a deep minimum around 2.5 Å, which was a rather unexpected result at this time. These results indicate that the connected triple (and possibly also quadruple) excitations are responsible for the formation of the bond. Reasons for such slow convergence of the traditional CI or CC expansions were analyzed in detail by Liu and McLean [22]. It was shown that the pathological behavior of this system encountered during studies performed with the single reference methods is mostly due to near degeneracy of the $2s$ and $2p$ orbitals of the beryllium atom. It gives the beryllium dimer a strongly multireference nature. By applying the multireference configuration interaction (MRCI) method, Liu and McLean found the interaction energy to be as large as 810 cm^{-1} and confirmed the existence of the minimum around 2.5 Å. These findings were later verified by several independent MRCI studies [23–30]. Therefore, it is now well established that Be_2 is *not* a van der Waals molecule.

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Since then, a large number of theoretical works entirely devoted to study of the beryllium dimer have been published and a more detailed bibliography is given elsewhere [31,32]. The interaction energy is typically determined to be within the range of 200–1000 cm^{-1} and it varies with the level of theory and quality of the basis sets used. However, it appears that in the most recent, and probably the most accurate, studies, the interaction energy fluctuates somewhere around 900 cm^{-1}. For instance, Martin [33] found $944 \pm 25\,cm^{-1}$, Gdanitz [34], 989 ± 8 cm^{-1}; Pecul *et al.* [35], $885\,cm^{-1}$; Reggen and Veseth [31], $945 \pm 15\,cm^{-1}$; Patkowski *et al.* [32], $938 \pm 15\,cm^{-1}$; Koput [36], $935 \pm 10\,cm^{-1}$; and Sharma *et al.*, 931.2 cm^{-1} [37]. Discrepancies between these results are still rather large, though, which indicates that the ground state of the beryllium dimer remains to be a challenge for modern quantum chemistry methods.

From the experimental point of view, the ground state of the beryllium dimer is also a demanding system. The first empirical confirmation of the fact that Be_2 is a deeply bound system, as theoretically predicted, was reported in the 1980s [38–40]. The most frequently cited experimental result for the well depth was given by Bondybey *et al.*, 790 ± 30 cm^{-1}. This result was not accurate and the true error is much larger than the estimated error bars. However, the discrepancy was not really due to the experimental error but mostly due to theoretical assumptions used to extract the dissociation energy. In fact, in 2006 Spirko [41] combined the experimental data of Bondybey with the best theoretical potential energy curve available at the time and refined the result to 923 cm^{-1}, which is much closer to the recent theoretical findings. In 2009 a new experiment was performed by Merritt *et al.* [42] and the interaction energy was found to be $929.7 \pm 2.0\,cm^{-1}$. Additionally, 11 vibrational levels were characterized [43]. Shortly afterwards, Patkowski *et al.* [44] suggested the existence of the 12th vibrational level, just 0.44 cm^{-1} below the dissociation limit, by using the "morphed" theoretical potential energy curve.

It is clear that the ground state of the beryllium dimer is a challenging system, with large requirements for the quality of the basis set and for the theoretical methods. Therefore, it is a good test case for the STOs combined with the state-of-the-art quantum chemistry methods. It is well known that STOs are able to satisfy the electron-nucleus cusp condition, thereby significantly improving the description of the wave function in the vicinity of the nuclei. This property makes STOs more reliable in calculations which depend crucially on the quality of the trial wave function in this regime, such as core-core and core-valence correlation effects, one-electron relativistic corrections of order α^2, etc. Other advantages of STOs are summarized at the end of the present paper. Notably, calculations with STO basis sets of quality up to sextuple ζ, aiming at spectroscopic accuracy, have never been performed thus far. In the case of such calculations special attention must be paid to technical issues, such as creation and benchmarking of basis sets, since the strategies adopted in case of Gaussian-type orbitals (GTOs) may not be straightforwardly transferable. In this paper we consider these issues in some detail but restrict ourselves to calculations at the equilibrium internuclear distance, R, equal to 2.4536 Å, which is the recent experimental value [42]. The whole potential energy curve will be reported later, along with a detailed study of the related spectroscopical issues.

This paper is organized as follows. In Sec. II we describe in detail the systematic construction of the STO basis sets. In Sec. III we present benchmarks for the beryllium atom which verify the reliability of the developed STO basis sets. Issues connected with extrapolations towards the complete basis set (CBS) are also investigated. In Sec. IV we present results for the ground state of the beryllium dimer. We calculate the valence and core correlations effects separately and estimate the corresponding errors. Additionally, we compute the values of the relativistic corrections and estimate the effects of the leading-order QED contributions. Finally, in Sec. V we conclude the paper and give a short outlook.

II. BASIS SETS

In the case of GTOs, the contracted functions are typically used to reproduce the Hartree-Fock energy first. Then, additional uncontracted functions are used to describe the electronic correlation; see the works of Dunning *et al.* [45–53] as a representative example. We found that GTO basis sets designed according to this principle somewhat lack flexibility for the $l = 0$ partial wave, especially in the molecular environment, since the number of uncontracted $1s$ orbitals is typically small. For ordinary GTO calculations this is not a problem, however, because correlation energy retrieved by $l = 0$ angular momentum functions is small, at least an order of magnitude below the contribution from $l = 1$ partial wave. Therefore, this lack of correlation coming from $l = 0$ functions is visible only for very accurate calculations where the contributions from more important partial waves are already sufficiently saturated. Since we aim at high-quality results, we do not use contractions of STOs.

There is also another important choice in the design of STO basis sets which is entirely absent in the case of GTO. For GTO calculations one typically uses only $1s$, $2p$, $3d$, etc., functions (with $n = l + 1$) since molecular integrals with these kinds of functions are particularly straightforward. In the case of STO one can use functions with $n > l + 1$ as well. For instance, in the case of $l = 0$ orbitals the expansion takes the form

$$\psi_i = e^{-\zeta_i r} \sum_k^{N_i} c_{ki}\, r^k, \tag{1}$$

where the value of ζ_i is characteristic for a given atomic shell. The expansion (1) is quite attractive, mainly because of a small number of nonlinear parameters which need to be optimized, only one per atomic shell, and very systematic enlargement towards the completeness through the parameters N_i. However, in practice we found that there are numerous problems connected with this expansion in our applications. The biggest drawback is the fact that basis sets constructed according to the principle (1) suffer from near-linear dependencies when N_i gets moderate or large. This effectively prohibits the construction of large basis sets close to completeness when the standard double precision arithmetic is used. Another problem is the fact that the expansion (1) is not as flexible as necessary, especially when transferred from atomic to a weakly bound molecular system.

TABLE I. Composition of STO basis sets for the beryllium atom.

Basis set	Atomic valence	Tight core	Diffuse
ATC-ETCC-1	$6s1p$	$1s$	$1s1p$
ATC-ETCC-2	$7s2p1d$	$1s1p$	$1s1p1d$
ATC-ETCC-3	$8s3p2d1f$	$2s2p1d$	$1s1p1d1f$
ATC-ETCC-4	$9s4p3d2f1g$	$2s3p2d1f$	$1s1p1d1f1g$
ATC-ETCC-5	$9s5p4d3f2g1h$	$3s4p3d2f1g$	$1s1p1d1f1g1h$
ATC-ETCC-6	$9s6p5d4f3g2h1i$	$3s5p4d3f2g1h$	$1s1p1d1f1g1h1i$

As a result, we found that more flexible and well-behaved basis sets can be obtained when the orbitals are expanded, similarly as for GTO, in a set of functions with $n = l + 1$ and their respective exponents are varied freely, i.e.,

$$\psi_i = \sum_k^{N_i} c_{ki}\, e^{-\zeta_{ik} r}. \tag{2}$$

This choice, however, brings up the problem of optimization of a large number of independent parameters ζ_{ik}. In the biggest basis set created in this work a direct use of Eq. (2) would require free optimization of several tens of the nonlinear parameters. This is possible but very time consuming. An even more daunting problem is the presence of a great number of local minima. There is no guarantee that a brute-force optimization would have found the true global minimum, even with a decent starting point. This fact puts the reliability of the extrapolation towards the CBS in question.

Aware of all the aforementioned issues, we adopted the strategy of *even tempering* so that the nonlinear parameters for a given angular momentum l are in the following form:

$$\zeta_{lk} = \alpha_l\, \beta_l^k \quad \text{with} \quad k = 0,1,2,\ldots. \tag{3}$$

Nowadays, even tempering is routinely applied for construction of GTO basis sets. However, this technique was originally proposed by Raffenetti and co-workers [54,55] in the context of STOs. Even tempering greatly reduces the number of independent parameters which need to be optimized (only two for each partial wave).

The first step in the creation of the STO basis sets is optimization of the atomic valence basis set. In this step the core $1s$ orbital of the beryllium atom is kept frozen and the CISD method, equivalent to FCI for the valence shell, is used. The optimization is carried out to minimize the *total* energy of the two-electron CISD, i.e., sum of the Hartree-Fock and CISD correlation energy.

Since the seminal work of Dunning and co-workers [45–53] it has been known that to allow for a reliable extrapolation towards CBS, basis sets need to be constructed according to the *correlation consistency* principle. Roughly speaking, it ensures that at a given stage all functions which give approximately the same energy contributions are simultaneously included. Our atomic valence basis sets are denoted ETCC-L, which stands for even-tempered correlation consistent and L is the largest angular momentum included. Therefore, ETCC-1 has the composition $6s1p$, ETCC-2 $7s2p1d$, and so forth, and only functions with $n = l + 1$ are used. The initial number of six $1s$ functions was found to be optimal. Compositions of all basis sets up to $L = 6$ are presented in Table I. At some point it becomes unnecessary to include more $1s$ functions, and thereafter their number was kept fixed. The even-tempered expansion (3) is used separately for each partial wave.

The second step in construction of the basis set for beryllium is addition of the "tight" functions which are necessary for description of the core-core and core-valence correlations. It is well known that the core electrons are chemically inert and their contribution to the total energy cancels out to a large extent when interaction energies are computed. This observation is the foundation for the so-called frozen-core approximation. However, in accurate calculations the frozen-core approximation cannot be applied, especially for an element such as beryllium. Obviously, valence basis sets cannot describe the core-core and core-valence correlations since polarization functions with large exponents, characteristic for the core, are absent. We added core polarization functions to the previously obtained ETCC-L basis sets. Detailed composition of the extended TC-ETCC-L basis sets (where TC stands for "tight core") is given in Table I for each L. In order to optimize the exponents of the core polarization functions, we minimized the difference between the total energies of all-electron CISD and frozen-core CISD for the beryllium atom. Since the number of independent nonlinear parameters was much smaller than for the valence basis sets, even tempering of the exponents was not necessary and all variables were optimized freely. A minor detail of the optimization procedure is that the derivative of the target function with respect to the logarithm of the exponent was used as a gradient, rather than the derivative with respect to the exponent itself. This stabilizes greatly the numerical performance of the optimization.

The third, and final, step of the basis sets creation is the addition of the diffuse functions. These functions are not necessary for the atomic calculations since tails of the electron density do not contribute greatly to the total energies of the atom. However, in a molecular environment tails of the electron density are responsible for the act of bonding in weakly interacting systems and accurate reproduction of the potential energy curve. Basis sets augmented with a set of diffuse functions are called A-ETCC-L, or ATC-ETCC-L in the case of the core-valence basis sets. A detailed structure of the augmented basis sets is given in Table I. Exponents of the diffuse functions were optimized to maximize the absolute value of the beryllium dimer interaction energy calculated with A-ETCC-L basis sets at the four-electron (valence) CCSD(T) level of theory [56].

Notably, the strategy that the diffuse functions are optimized to maximize the absolute value of the interaction energy makes

them formally dependent on the internuclear distance, R. This is, in fact, exactly in line with our intentions. In this work we consider only one value of R, corresponding to the minimum of the potential energy curve, so that there is no ambiguity in how the calculations are carried out. In a case where a complete potential energy curve is required, diffuse functions can be optimized for several values of R and then interpolated smoothly. The present approach is inspired by the works of Kołos and co-workers concerning the hydrogen molecule [57–60]. Basis sets used in these works contained several nonlinear parameters which were handled in a manner similar to that described above and no significant difficulties were reported.

All optimizations necessary to construct the basis sets were carried out by using a pseudo-Newton-Rhapson method with an approximate update of the Hessian matrix [61]. Our own code, written especially for this purpose, was used throughout. This program is interfaced with the GAMESS package [62,63], which carries out the electronic structure calculations. A gradient with respect to nonlinear parameters was calculated numerically with the two-point finite difference formula. Close to a minimum, where more accurate values of the gradient are necessary, the four-point finite difference formula was applied. Optimization was stopped when the energy differences between two consecutive iterations fell below 1 nH and the largest element of the gradient fell below 10 μH, simultaneously. Typically, several tens of iterations were necessary to converge to a minimum in the biggest calculations. To avoid the exponent values of two functions collapsing, which occasionally happened, a Gaussian-type penalty function was applied routinely.

STOs constitute a convenient basis set for calculation of the relativistic corrections because of the cusp at the origin. Nonetheless, it is obvious that standard STO basis sets used in calculation of the Born-Oppenheimer potential may not be fully satisfactory. To overcome this problem we modified our ATC-ETCC-L basis sets by replacing all 1s orbitals with a new set, common for each L. The latter consists of 15 functions and was trained to minimize the Hartree-Fock energy of the beryllium atom. The value obtained, −14.573 023 138 5, differs at the 10th significant digit from the best estimate available in the literature, −14.573 023 168 305 [64]. The s-extended basis sets are abbreviated as ATC-ETCC-L+S.

Composition of the STO basis sets along with detailed values of the exponents and quantum numbers are given in the Supplemental Material [65].

III. ATOMIC BENCHMARKS

A. Nonrelativistic energy

The beryllium atom is a convenient system for benchmarking purposes because accurate reference values of the total energies and relativistic corrections are available in the literature. Therefore, before the calculations on the diatomic system are given, it is useful to check the adequacy of the strategy and the performance of our basis sets in the atomic case. We calculated the FCI energies of the beryllium atom by using ATC-ETCC-L basis sets with $L = 2, \ldots, 6$. A general FCI program HECTOR [66], written by one of us (M.P.), was used for this purpose. The starting Hartree-Fock orbitals were taken from the GAMESS program package, interfaced with our STO integral code.

TABLE II. Total energy, E_{total}, and the correlation energy, E_c, of the beryllium atom calculated at the FCI level of theory by using the STO basis sets ATC-ETCC-L. The limit of the Hartree-Fock energy is assumed to be -14.573 023 H.

Basis set	E_c/mH	E_{total}/H
ATC-ETCC-2	−85.976	−14.658 998
ATC-ETCC-3	−91.479	−14.664 502
ATC-ETCC-4	−92.994	−14.666 017
ATC-ETCC-5	−93.608	−14.666 631
ATC-ETCC-6	−93.902	−14.666 925
CBS	−94.322	−14.667 345
Pachucki and Komasa [71]	−94.333	−14.667 356

In Table II we present the FCI results for the beryllium atom. It is important for further developments to extrapolate these results towards the CBS limit. Many extrapolation methods were suggested in the literature [67–70], but the following formula was found to be particularly reliable for the estimation of the CBS limit of the correlation energy,

$$E = A + \frac{B}{L^3} + \frac{C}{L^5}, \tag{4}$$

where L is the largest angular momentum present in the basis set. The Hartree-Fock results were not extrapolated but simply the value in the biggest basis set was taken. Extrapolation of the results given in Table II leads to the result −14.667 345 for the total energy of the beryllium atom. This can be compared with the reference value, obtained by Pachucki and Komasa [71] by using an explicitly correlated four-electron basis set, −14.667 356, and the error is equal to 11 μH. Remarkably, the extrapolation reduces the error by an order of magnitude, compared with the largest basis set available. In fact, we found that an essential feature of STO basis sets is that they provide very reliable extrapolation towards the CBS limit, as compared with GTO basis sets of a similar quality.

B. One-electron relativistic corrections

The leading relativistic corrections (the second order in the fine structure constant, α) to the energy of light systems can be computed perturbatively as an expectation value of the Breit-Pauli Hamiltonian [72]. For a molecule in a singlet state, this correction is [73,74]

$$E^{(2)} = \langle P_4 \rangle + \langle D_1 \rangle + \langle D_2 \rangle + \langle B \rangle, \tag{5}$$

$$\langle P_4 \rangle = -\frac{\alpha^2}{8} \left\langle \sum_i \nabla_i^4 \right\rangle, \tag{6}$$

$$\langle D_1 \rangle = \frac{\pi}{2} \alpha^2 \sum_a Z_a \left\langle \sum_i \delta(\mathbf{r}_{ia}) \right\rangle, \tag{7}$$

$$\langle D_2 \rangle = \pi \alpha^2 \left\langle \sum_{i>j} \delta(\mathbf{r}_{ij}) \right\rangle, \tag{8}$$

$$\langle B \rangle = \frac{\alpha^2}{2} \left\langle \sum_{i>j} \left[\frac{\boldsymbol{\nabla}_i \cdot \boldsymbol{\nabla}_j}{r_{ij}} + \frac{\mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \boldsymbol{\nabla}_j) \boldsymbol{\nabla}_i}{r_{ij}^3} \right] \right\rangle, \tag{9}$$

where $\langle\hat{\mathcal{O}}\rangle = \langle\Psi|\hat{\mathcal{O}}|\Psi\rangle$. The consecutive terms in the above expression are the mass-velocity $\langle P_4\rangle$, one-electron Darwin $\langle D_1\rangle$, two-electron Darwin $\langle D_2\rangle$, and Breit $\langle B\rangle$ corrections, respectively. We assume that the value of the fine structure constant, α, is 1/137.035 999 7, as recommended by CODATA [75].

Let us consider the values of the one-electron relativistic corrections, $\langle P_4\rangle$ and $\langle D_1\rangle$. They can easily be obtained within the STO framework, since the corresponding one-electron integrals are fairly straightforward to compute. Integrals including the one-electron Dirac δ distribution reduce to the values of STOs at a given point of space which is elementary. Integrals including the ∇^4 operator reduce to combinations of the ordinary overlap integrals over STOs. General subroutines for calculation of the aforementioned integrals are now a part of our STO integral package. Note that $\langle P_4\rangle$ and $\langle D_1\rangle$ corrections (called also collectively the Cowan-Griffin contribution [76]) are very sensitive to the quality of the wave function in the vicinity of the nuclei. Therefore, their evaluation by using the STO basis set is supposed to be particularly advantageous.

In Table III we present values of the one-electron relativistic corrections, calculated with s-extended STO basis sets. The results are compared with the values reported recently [71], which are considered "exact" in the present context. Remarkably, in the biggest basis set, ATC-ETCC-6+S, the relative error of our values compared with the accurate ones is only ≈0.03% and ≈0.003% for $\langle P_4\rangle$ and $\langle D_1\rangle$, respectively. Moreover, even in the smallest basis set, ATC-ETCC-2+S, these errors increase to only about 0.1% and 0.005%. We found that it is impossible to reach a similar level of accuracy with the available (decontracted) GTO basis sets, and typically the resulting error is (at least) an order of magnitude larger.

It is also interesting to perform extrapolations of the values of one-electron relativistic corrections towards CBS. We found empirically that the following formulas provide the best fit:

$$A + \frac{B}{(L+1)^2} \quad \text{for} \quad P_4, \tag{10}$$

$$A + \frac{B}{(L+1)^4} \quad \text{for} \quad D_1. \tag{11}$$

Results of the extrapolations from $L = 3, 4, 5, 6$ are presented in Table III. The extrapolation reduces the error of the mass-velocity correction to 0.02%, but increases it insignificantly for the one-electron Darwin correction.

TABLE III. Mass-velocity, $\langle P_4\rangle$, and one-electron Darwin, $\langle D_1\rangle$, corrections for the beryllium atom at the FCI level of theory. The factor of α^2 is not included. All values are given in atomic units.

Basis set	$\langle P_4\rangle$	$\langle D_1\rangle$
ATC-ETCC-2+S	−270.431 854	222.218 606
ATC-ETCC-3+S	−270.527 702	222.225 660
ATC-ETCC-4+S	−270.568 886	222.232 142
ATC-ETCC-5+S	−270.594 238	222.234 514
ATC-ETCC-6+S	−270.609 955	222.235 299
CBS	−270.648 568	222.236 568
Pachucki and Komasa [71]	−270.704 68(25)	222.229 35(13)

IV. BERYLLIUM DIMER

A. Four-electron (valence) contribution

From earlier studies of the beryllium dimer, it is well known that a major contribution to the interaction energy comes from the correlations between valence electrons. Freezing both $1s$ atomic orbitals makes the dimer effectively a four-electron system which can be successfully treated with FCI method in large basis sets. We performed the frozen-core FCI calculations in basis sets A-ETCC-L with $L = 2, \ldots, 6$. The Abelian group, D_{2h}, was used in computations. We believe these are the biggest valence FCI calculations ever performed for this system in terms of the number of configurations included in construction of the Hamiltonian matrix. The results of the calculations are included in Table IV. In all cases the counterpoise (CP) correction for the basis set superposition error (BSSE) was applied [77]. It is clear, that the results are slowly convergent with respect to the quality of the basis set. This is probably due to the fact that bonding significantly perturbs the atomic densities. The increment of the interaction energy between $L = 5$ and $L = 6$ basis sets is as large as 11.9 cm^{-1}, suggesting that the CBS value is still significantly below the $L = 6$ value.

Because of this observation it is necessary to perform some kind of extrapolation towards the CBS. The correlation energy alone was the subject of the extrapolation, separately for the atom and for the dimer. We used the formula (4) which was previously used successfully for the atomic calculations. We also observe that in the largest basis set, the Hartree-Fock (HF) results are already converged at least to eight significant digits. It is therefore unnecessary to extrapolate the HF results and simply the value obtained in $L = 6$ basis was taken as the CBS result.

Note that the CBS increment found in the extrapolation of the correlation energy is quite substantial and crucial for the final results. It amounts to as much as nearly 20 cm^{-1} in the interaction energy. Thus, it is necessary to additionally verify the reliability of the extrapolation. To do so, we first performed the extrapolation from $L = 2$, 3, 4, 5 basis sets in order to estimate the $L = 6$ value. The extrapolated $L = 6$ value gives the interaction energy equal to 847.4 cm^{-1}, whereas the corresponding true calculated result is 845.7 cm^{-1}. The difference, amounting to 1.7 cm^{-1}, is assumed to be also the error of the CBS extrapolation from $L = 2$, 3, 4, 5, 6. The quality of the extrapolation for the dimer is illustrated at Fig. 1. A quite similar excellent fit was obtained for the atomic calculations. Finally, our best estimate for the valence contribution to the interaction energy is 864.9 ± 1.7 cm^{-1}. Note that this error estimation is a conservative one because extrapolation from a larger number of points can be expected to be more reliable. Additionally, the increment in the interaction energy between $L = 4$ and $L = 5$ basis sets is significantly larger than between $L = 5$ and $L = 6$ or between $L = 6$ and the estimated CBS. Therefore, it is possible that our extrapolated result is more accurate than we assume here.

TABLE IV. Results of the four-electron valence FCI calculations for the beryllium dimer at the internuclear distance 2.4536 Å. N_b denotes the number of basis set functions, N_{SD} is the dimension of the Hamiltonian matrix in A_g symmetry, E_{HF} is the Hartree-Fock energy, E_c is the correlation energy at FCI level, CP is the CP correction (for BSSE) to the interaction energy, and D_e is the calculated CP-corrected FCI interaction energy. The values in the last row are the extrapolated CBS values (see the main text for the discussion). All values are given in the atomic units unless stated otherwise.

Basis set	N_b	N_{SD}	E_{HF}	E_c	CP (cm^{-1})	D_e (cm^{-1})
A-ETCC-2	54	237 548	−29.133 941 8	−0.104 687 3	12.5	273.8
A-ETCC-3	100	2 895 037	−29.134 162 1	−0.107 057 4	8.3	710.6
A-ETCC-4	168	23 685 257	−29.134 174 5	−0.107 639 2	4.1	802.9
A-ETCC-5	260	138 002 229	−29.134 175 1	−0.107 850 5	2.6	833.8
A-ETCC-6	384	663 593 429	−29.134 175 4	−0.107 942 3	1.8	845.7
CBS	∞	∞	−29.134 175 4	−0.108 069 5	0.0	864.9 ± 1.7

Our final result, namely 864.9 ± 1.7 cm^{-1}, is in line with recent findings of other authors. Patkowski *et al.* [32] found 857 ± 12 cm^{-1}, if we follow their method of error estimation, and Martin [33] gives 872 ± 15 cm^{-1}. The present result lies well within the error bounds obtained in these works. A slight discrepancy is found between our result and the value recently reported by Evangelisti and co-workers [78], who give 850.4 cm^{-1} without any error estimation. We believe that this result is inaccurate, mainly because lack of the diffuse functions in their GTO basis set. Notably, our error bounds, which are conservative anyway, are an order of magnitude smaller than those obtained in the aforementioned works.

B. Core-core and core-valence contributions

The second step in our calculations is a reliable determination of the core-core and core-valence contribution to the interaction energy. This task, however, is far from being trivial. A brief inspection of values available in the literature reveals that estimations from 65 cm^{-1} [78] to as large as 89 cm^{-1} [31] were obtained. Because of the fulfillment of the nuclear cusp condition, the STO basis used in the present work can be expected to be more suitable for the description of core region than the GTOs used thus far.

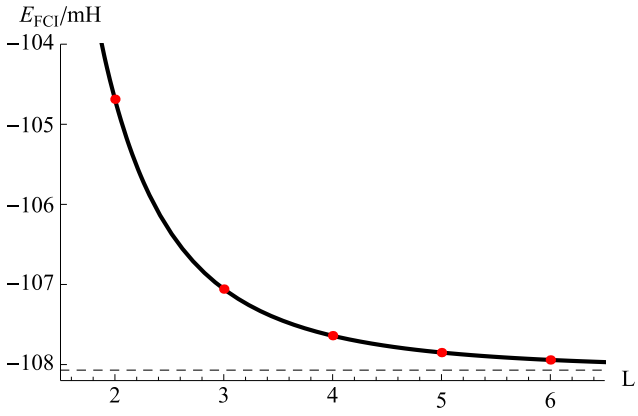

FIG. 1. (Color online) Quality of the extrapolation towards the CBS for the beryllium dimer using results from basis sets A-ETCC-L with $L = 2, \ldots, 6$ based on the theoretical expression (4). The dashed line denotes the estimated limit.

Our preliminary study suggests that the CCSDT model is a particularly good method for the estimation of the inner-shell contribution. The effect of connected quadruple excitations was found to be very small in this case. In fact, the effect of quadruples can be highly overestimated in small basis sets but quickly diminishes when the basis set is enlarged. We found this particular behavior in virtually any approximate quadruples method that was available to us. Therefore, we can conclude that the CCSDT method in the CBS limit would probably give the core-core and core-valence contribution accurate to within a few tenth of cm^{-1}. A similar observation was also made implicitly by Martin [33].

Unfortunately, we are able to perform all-electron CCSDT calculation only in ATC-ETCC-L basis sets with $L = 2$, 3, 4. The results are 31.5, 56.7, and 63.9 cm^{-1}, respectively. CBS extrapolation from these values can be performed by using formula (4), giving 69.6 cm^{-1}. However, this three-point extrapolation is not particularly trustworthy since the CBS increment is rather large and no reliable error estimation can be given. Thus, we must seek some approximate method, with smaller computational costs, giving results comparable to CCSDT in the CBS limit.

In Table V we show inner-shell contributions to the interaction energy computed at various levels of theory. CCSD, CCSD(T), and MP2 calculations were performed with the GAMESS package, while CCSDT and MP4 energies were evaluated with the help of the ACESII program [79]. All values in this table were obtained by subtracting the interaction energy obtained with the frozen-core approximation from the corresponding all-electron values. Let us compare the results of MP4 and CCSD(T) with the complete CCSDT model. One sees that the MP4 method slightly underestimates the inner-shell

TABLE V. Core-core and core-valence contributions to the interaction energy computed at various levels of theory. All values are given in cm^{-1}. Extrapolations are performed according to formula (4), for the atom and dimer separately, using the CP-corrected data.

Basis set	N_b	CCSD	CCSDT	CCSD(T)	MP2	MP4
ATC-ETCC-2	62	28.2	31.5	39.0	−34.0	28.9
ATC-ETCC-3	126	50.4	56.7	61.2	57.2	56.4
ATC-ETCC-4	224	55.7	63.9	66.4	63.6	63.5
ATC-ETCC-5	364	57.4		67.7	65.7	65.7
CBS	∞	59.3	69.6	69.5	67.8	68.4

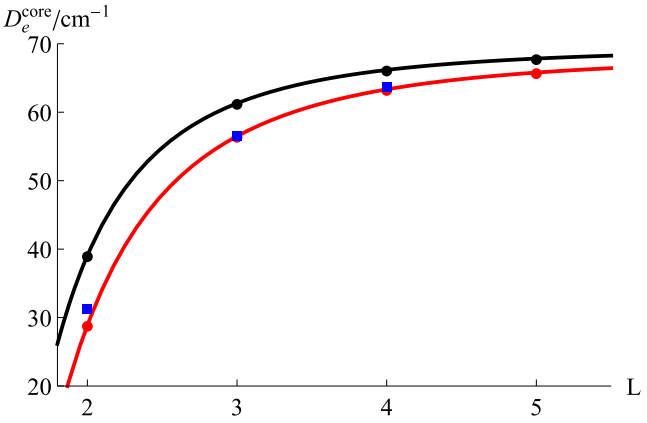

FIG. 2. (Color online) Contribution of the inner-shell effects to the interaction energy, denoted shortly D_e^{core}, calculated by using ATC-ETCC-L basis sets. Black dots are the CCSD(T) results and the black line is the CCSD(T)/CBS extrapolation curve. Analogously, red dots are the MP4 results and the red line is the corresponding CBS extrapolation. Blue squares are the available CCSDT results, for $L = 2, 3, 4$.

contribution compared to CCSDT while the CCSD(T) model overestimates it significantly, especially in smaller basis sets. Note additionally that MP4 and CCSD(T) results strictly bracket the CCSDT values, as illustrated in Fig. 2. If we assume that this behavior holds further, then the CBS limit of the CCSDT method should lie between the corresponding limits of MP4 and CCSD(T). Fortunately, the CBS limit is 68.4 and 69.5 cm^{-1} for MP4 and CCSD(T), respectively. The exact result probably lies between these values so as the final result we take the average of the two and estimate the error as a half of the difference between them. This gives the final value of the core-core and core-valence contributions to the interaction energy equal to 69.0 ± 0.6 cm^{-1}. The small effect of the connected quadruples contribution is probably already incorporated in the error estimation.

Note that the final value determined by us is significantly smaller than some of the estimations given in the literature. For instance, Martin gives 76.2 cm^{-1} [33], while Patkowski *et al.* [32] reports as much as 85 ± 5 cm^{-1}. We believe that these discrepancies are mainly due to defects in the GTO basis sets used by authors. In fact, when GTO basis sets are not designed very carefully in the core region, the inner-shell correlation effects can be significantly overestimated. Naturally, STOs are much more appropriate in this respect, which is one of their noteworthy advantages.

C. Relativistic, QED, and adiabatic corrections

One-electron relativistic corrections were evaluated by using the s-extended basis sets, described in Sec. II. The results are presented in Table VI. Calculations of the one-electron expectation values, at the all-electron and frozen-core CCSD level of theory, were performed by using a Λ operator technique [80–83] implemented by default in the GAMESS package. Relaxation of the HF orbitals is neglected in CCSD calculations. FCI calculations were done using our own program and the expectation values are straightforward to evaluate by using the FCI wave functions.

Extrapolations are carried out by using the empirical formula (10) for *both* $\langle D_1 \rangle$ and $\langle P_4 \rangle$. Our strategy for evaluation of the contribution to the interaction energy from the Cowan-Griffin approximation [76] is as follows. We use the valence FCI values corrected for the core-core and core-valence effects as a difference between all-electron and frozen-core CCSD results. It was found previously that CCSD method behaves reasonably for the inner-shell correlations (see Table V) and this accuracy is sufficient for the present purposes. In Table VII we present contributions to the interaction energy from $\langle D_1 \rangle$ and $\langle P_4 \rangle$ corrections, calculated at this level of theory. The core-core and core-valence CCSD effect is estimated to be –0.4 cm^{-1}, while the pure valence FCI contribution is –4.4 cm^{-1}. By summing both corrections we obtain -4.8 ± 0.2 cm^{-1} for the final contribution to the interaction energy coming from the one-electron relativistic corrections. The error is simply taken as the (rounded up) value of the corresponding CBS increment. The obtained value is in a moderate agreement with the values given by Patkowski *et al.* [32], –4.1 cm^{-1}, Martin [33], –4.0 cm^{-1}, and Gdanitz [34], –5.2 cm^{-1}. However, as far as we can tell, these values are not extrapolated and the authors report no respective error bars of their result. We believe that our final values are much more accurate due to the fact that STO basis sets were used throughout.

Let us now focus on the two-electron relativistic corrections: two-electron Darwin, $\langle D_2 \rangle$, and Breit, $\langle B \rangle$, contributions. Evaluation of the latter correction within the STO basis set is not feasible at present. This is mostly due to the fact the matrix elements of the Breit term, Eq. (5), are extremely difficult to compute with the exponential functions. As far as we know, the only accurate molecular calculations of the Breit

TABLE VI. Mass-velocity, $\langle P_4 \rangle$, and one-electron Darwin, $\langle D_1 \rangle$, corrections for the beryllium dimer calculated at the CCSD and FCI levels of theory. The factor of α^2 is not included. All values are given in the atomic units.

	All-electron CCSD		Frozen-core CCSD		Frozen-core FCI	
Basis set	$\langle P_4 \rangle$	$\langle D_1 \rangle$	$\langle P_4 \rangle$	$\langle D_1 \rangle$	$\langle P_4 \rangle$	$\langle D_1 \rangle$
ATC-ETCC2+S	−539.847 891	443.692 152	−537.394 631	443.278 203	−537.133 303	443.083 762
ATC-ETCC3+S	−539.971 064	443.675 656	−537.333 536	443.241 928	−537.036 087	443.021 849
ATC-ETCC4+S	−540.030 590	443.664 899	−537.317 658	443.233 044	−537.014 183	443.008 427
ATC-ETCC5+S	−540.073 538	443.665 227	−537.310 464	443.229 426	−537.004 508	443.003 144
CBS	−540.141 465	443.655 919	−537.305 424	443.226 021	−536.995 150	442.996 653

TABLE VII. Contributions to the interaction energy of the beryllium dimer from the mass-velocity, $\langle P_4 \rangle$, and one-electron Darwin, $\langle D_1 \rangle$, corrections calculated at the CCSD and FCI levels of theory. All results are given in cm^{-1}.

	All-electron CCSD			Frozen-core CCSD			Frozen-core FCI		
Basis set	$D_e(P_4)$	$D_e(D_1)$	ΣD_e	$D_e(P_4)$	$D_e(D_1)$	ΣD_e	$D_e(P_4)$	$D_e(D_1)$	ΣD_e
ATC-ETCC2+S	−12.40	9.28	−3.12	−11.87	8.87	−3.00	−14.93	11.14	−3.78
ATC-ETCC3+S	−13.35	9.79	−3.57	−12.71	9.41	−3.30	−16.19	11.98	−4.21
ATC-ETCC4+S	−13.63	10.08	−3.54	−12.94	9.56	−3.38	−16.49	12.18	−4.30
ATC-ETCC5+S	−13.72	10.14	−3.58	−13.03	9.61	−3.42	−16.60	12.25	−4.35
CBS	−14.26	10.44	−3.81	−13.10	9.67	−3.44	−16.73	12.34	−4.39

term within the exponential basis set were performed by Kołos and Wolniewicz [59,84] for various electronic states of H_2.

Because of these difficulties, we calculated $\langle D_2 \rangle$ and $\langle B \rangle$ in GTO basis sets. It will be shown that contributions of the two-electron relativistic corrections are small and GTO basis sets are sufficient to meet the prescribed accuracy requirements.

For calculations of the two-electron relativistic corrections we used modified aug-cc-pCVXZ series of GTO basis sets [45–53]. To improve the quality of the wave function the standard set of $1s$ GTO orbitals was replaced with a new one comprising 23 $1s$ functions. This set was obtained by minimizing the HF energy of the beryllium atom. Apart from that, the original $1s$ diffuse functions from the initial aug-cc-pCVXZ basis sets were kept. We also decontracted the $2p$ polarization functions and removed the redundant orbitals. Higher angular momentum shells were neither modified nor decontracted.

The DALTON program package [85] was used for CCSD(T) calculations and our own program for the valence FCI calculations. In Table VIII we show contributions of $\langle D_2 \rangle$ and $\langle B \rangle$ to the interaction energy computed at three different levels of theory: all-electron and frozen-core CCSD(T) and frozen-core FCI. It is not necessary to perform CBS extrapolations since the contributions to the interaction energy are converged to about 0.01–0.02 cm^{-1} already in the biggest basis set. We take the frozen-core FCI contribution as our result and additionally correct it for the inner-shell effects as a difference between the all-electron and frozen-core CCSD(T) values. In this way, we obtain the contribution to the interaction energy from the two-electron relativistic correction equal to –0.5 cm^{-1}. The error can be estimated to be much below 0.1 cm^{-1} by observing the convergence pattern in the available basis sets. Unfortunately, we are not aware of any available literature values that we could compare with.

By summing the computed one- and two-electron relativistic contributions, we find that α^2 effects decrease the interaction energy by 5.3 ± 0.2 cm^{-1}. This contribution is quite sizable and definitely needs to be included to obtain a spectroscopically accurate potential energy curve for the beryllium dimer.

Let us now pass to the leading-order QED contribution. Theoretically, this effect should be by a factor α smaller than the Breit-Pauli contribution and thus entirely negligible within the present accuracy requirements. However, it turns out that among the relativistic contributions to the interaction energy there is a significant cancellation between $\langle P_4 \rangle$ and $\langle D_1 \rangle$ terms, so that the result is an order of magnitude smaller than the net values of separate terms. Therefore, the leading QED corrections may still contribute to the interaction energy significantly. In fact, this situation was previously encountered in calculations for the dihydrogen [86] and the helium dimer [87]. This suggests that whenever the α^2 relativistic corrections are included in accurate calculations for light systems, the leading-order QED contributions should also be at least estimated.

The leading QED correction (of the order α^3 and $\alpha^3 \ln \alpha$) to the electronic energy of a molecular singlet state takes the form [88,89]

$$E^{(3)} = \frac{8\alpha}{3\pi}\left(\frac{19}{30} - 2\ln\alpha - \ln k_0\right)\langle D_1 \rangle + \frac{\alpha}{\pi}\left(\frac{164}{15} + \frac{14}{3}\ln\alpha\right)\langle D_2 \rangle + \langle H_{\mathrm{AS}} \rangle, \quad (12)$$

where $\ln k_0$ is the so-called Bethe logarithm [72,90] and $\langle D_1 \rangle$ and $\langle D_2 \rangle$ are the values of the one- and two-electron Darwin corrections (including the factor of α^2). The term $\langle H_{\mathrm{AS}} \rangle$ is the Araki-Sucher contribution, given by the expectation value

$$\langle H_{\mathrm{AS}} \rangle = -\frac{7\alpha^3}{6\pi}\left\langle \sum_{i>j} \hat{P}\left(r_{ij}^{-3}\right) \right\rangle, \quad (13)$$

TABLE VIII. Contributions to the interaction energy of the beryllium dimer from the two-electron Darwin, $\langle D_2 \rangle$, and Breit, $\langle B \rangle$, corrections calculated at the CCSD(T) and FCI levels of theory within GTO basis sets. All results are given in cm^{-1}.

	All-electron CCSD(T)			Frozen-core CCSD(T)			Frozen-core FCI		
Basis set	$D_e(D_2)$	$D_e(B)$	ΣD_e	$D_e(D_2)$	$D_e(B)$	ΣD_e	$D_e(D_2)$	$D_e(B)$	ΣD_e
aug-cc-pCVDZ	0.38	−0.82	−0.44	0.41	−0.73	−0.32	0.42	−0.76	−0.34
aug-cc-pCVTZ	0.42	−0.89	−0.47	0.46	−0.77	−0.32	0.46	−0.80	−0.34
aug-cc-pCVQZ	0.43	−0.90	−0.47	0.47	−0.79	−0.31	0.48	−0.82	−0.34
aug-cc-pCV5Z	0.44	−0.91	−0.47	0.48	−0.79	−0.31	0.48	−0.82	−0.34

and $\hat{P}(r_{ij}^{-3})$ denotes the regularized r_{ij}^{-3} distribution

$$\left\langle \hat{P}\left(r_{ij}^{-3}\right)\right\rangle = \lim_{a\to 0}\left\langle \theta(r_{ij}-a)r_{ij}^{-3} + 4\pi(\gamma_E + \ln a)\delta(\mathbf{r}_{ij})\right\rangle, \quad (14)$$

where γ_E is the Euler-Mascheroni constant. It is well known that computation of the Bethe logarithm and Araki-Sucher terms is extremely difficult and has never been attempted for any molecular system apart from the dihydrogen [86] and the helium dimer [87]. Therefore, we have to adopt some approximate strategy for determination of $E^{(3)}$. Fortunately, except at very large R, the Araki-Sucher term is small compared to the overall leading-order QED correction and thus can be neglected. The Bethe logarithm, on the other hand, was found to vary insignificantly as the function of R, when R is moderate (or large), for the helium dimer and dihydrogen. Therefore, the asymptotic (atomic) value of the Bethe logarithm can be adopted.

A very accurate value of $\ln k_0$ for the beryllium atom has been given recently by Pachucki and Komasa [71], $\ln k_0 = 5.750\,34$. We use the extrapolated values of $\langle D_1\rangle$ and $\langle D_2\rangle$, equal to 0.023 613 and 0.000 522 for the dimer and 0.011 836 and 0.000 262 for the monomer, respectively. With these assumptions, contribution of the lowest-order QED effects to the interaction energy of the beryllium dimer is calculated to be 0.37 cm^{-1}. This value is an order of magnitude smaller than the relativistic corrections, as expected. However, its omission would significantly increase the total error of our theoretical predictions. It is difficult to estimate strictly what is the effect of the adopted approximations on the value of QED contribution to the interaction energy. For the dihydrogen molecule, exactly the same approximations introduce an error slightly less than 10%, based on the results presented in Ref. [86]. Therefore, we can assume very conservatively that error of the present calculations is at most 20%. This finally gives us estimation of the leading-order QED contribution to the interaction energy equal to 0.4 ± 0.1 cm^{-1}.

We also check the next higher-order QED contribution. It is well known from the calculations on the helium atom [91,92], that the α^4 effects are dominated by the one-loop term [93] given by

$$E^{(4)}_{\mathrm{one-loop}} = 16\alpha^2\left(\frac{427}{192} - \ln 2\right)\langle D_1\rangle, \quad (15)$$

in the case of the beryllium atom (or dimer). The above quantity is a scaled one-electron Darwin correction and thus can be easily computed. We found the contribution to the interaction energy of the one-loop term to be approximately 0.017 cm^{-1}, which is well below 0.1 cm^{-1}. Therefore, as anticipated, the higher-order QED contributions can safely be neglected within the present accuracy requirements. This additionally gives a verification that the QED perturbative series converges rapidly for the beryllium dimer.

The remaining missing part of the theory that has to be investigated is the finite nuclear mass, i.e., the adiabatic correction. We calculated this correction with help of the CFOUR [94] and MRCC [95,96] program packages at both all-electron and frozen-core CCSD and CCSDT levels of theory [97]. The GTO basis sets which were previously used for computation of the two-electron relativistic corrections were utilized. In all cases we found that the contribution to the interaction energy from the adiabatic correction was significantly below 0.1 cm^{-1}. In fact, the net values of the adiabatic correction for both atom and dimer were large, but they canceled out almost to zero. This is probably due to the fact that the adiabatic correction contribution to the interaction energy as a function of the internuclear distance, R, crossed zero near the value of R adopted by us (close to the minimum). A similar situation was found in the case of the helium dimer [87]. Our observation is additionally verified by calculations of Koput [36], who found that contribution of the adiabatic correction to the interaction energy varies by only 2 cm^{-1} along the whole potential energy curve. As a result, we assume that the contribution to the interaction energy coming from the adiabatic effects is equal to zero. We estimate that the error of this result is at most 0.1 cm^{-1}.

TABLE IX. Final error budget of the calculations for the ground state ($^1\Sigma_g^+$) of the beryllium dimer obtained in this work. All values are given in cm^{-1}.

	Contribution to D_e
Valence correlations	$+864.9 \pm 1.7$
Inner-shell correlations	$+69.0 \pm 0.6$
Relativistic (α^2) effects	-5.3 ± 0.2
Leading-order (α^3) QED effects	$+0.4 \pm 0.1$
Adiabatic correction	$+0.0 \pm 0.1$
Total	$+929.0 \pm 1.9$
Experiment	$+929.7 \pm 2.0$

D. Total interaction energy

All contributions to the interaction energy of the beryllium dimer computed in this work are listed in Table IX. By summing all contributions we obtain the value 929.0 cm^{-1}, which is the main result of our study. The overall error of the calculations is estimated by summing squares of all fractional errors (1.7, 0.6, 0.2, 0.1, 0.1 cm^{-1}) and taking the square root, which gives 1.9 cm^{-1} (rounded up) or 0.2%. The total result, 929.0 ± 1.9 cm^{-1}, is in very good agreement with the latest experimental value, 929.7 ± 2.0 cm^{-1}, reported by Merritt *et al.* [42]. In fact, the present result lies within the error bars of the empirical value and *vice versa*.

Let us also comment on the timings of the present calculations. It is true that any gain connected with the use of STOs can easily diminish if computation of the STO two-electron integral files becomes overwhelmingly time consuming, up to a point when it is more expensive than evaluation of the correlation energy. There is such a risk, because STO integral algorithms are inherently more complicated and demanding than their GTO counterparts. In fact, we found that calculation of the STO integrals is one or two orders of magnitude more expensive than in the case of GTOs, with the same size of the basis set. This sounds daunting but the actual situation is more complex. For instance, in the largest basis sets used in this work, the calculation of the GTO two-electron integrals is a matter of several minutes, while in STOs it takes up to few hours. However, full CI or high-level CC calculations typically take several days to converge. Therefore, calculation of the integral files constitutes a small fraction of the total timing and does not pose any practical bottleneck. This is clearly a

TABLE X. Results of the selected theoretical predictions for the ground state of the beryllium dimer published since the late 1990s. All values are given in cm^{-1} and error bars are shown if estimated originally. Relativistic corrections are included if calculated. AE and FC denote all-electron and frozen-core, respectively. A majority of the acronyms appearing below is explained in the main text, apart from the following: ACPF, averaged coupled-pair functional; CC3, CC model with an approximate treatment of triple excitations; CAS, complete active space; MR-CISD+Q, MRCI with single and double excitations; Q denotes a specific Davidson-type correction for lack of size extensivity.

Year	Method	D_e	Reference
1999	FC CCSD(T)+FCI/CBS and AE CAS-ACPF	944 ± 25	Martin [33]
1999	CAS r_{12}-MR-ACPF/GTO($19s11p6d4f3g2h$)	898 ± 8	Gdanitz [34]
2000	CC3+FCI/d-aug-cc-pVQZ	885	Pecul *et al.* [35]
2005	EXRHF/GTO($23s10p8d6f3g2h$)	945 ± 15	Røggen and Veseth [31]
2007	AE CCSD(T)/CBS and FC FCI/CBS	938 ± 15	Patkowski *et al.* [32]
2007	Variational Monte Carlo and fixed-node diffusion Monte Carlo	829 ± 64	Harkless and Irikura [98]
2010	FC FCI/CBS and AE MR-CISD+Q	912	Schmidt *et al.* [27]
2010	AE MRCI/CBS	818	Mitin [28]
2011	AE CCSD(T)/CBS and FC FCI/CBS	935 ± 10	Koput [36]
2013	FC FCI/CBS and AE CCSD(T)/cc-pV6Z	927.4 ± 12	Evangelisti *et al.* [78]
2014	Density matrix renormalization group (DMRG)	931.2	Sharma *et al.* [37]
Present	FC FCI/CBS and AE CCSD(T)/MP4/CBS	929.0 ± 1.9	

consequence of relatively low scaling (N^4) of the calculations of the integral files, as compared with high-level CC of FCI methods.

It is also worth comparing our results with the latest theoretical values predicted by other authors. In Table X we collected most of the theoretical results published in the late 1990s and since then. An extensive bibliography of calculations published prior to this date can be found in Refs. [31] and [32]. Probably the most reliable calculations given thus far for the beryllium dimer are those of Patkowski *et al.* [32], giving $938 \pm 15\ cm^{-1}$, and Koput [36], $935 \pm 10\ cm^{-1}$. Our result is slightly lower but it lies within the error bars estimated by authors. Remarkably, the error predicted by us is by an order of magnitude smaller than in the previous works, despite that our estimations were rather conservative. Therefore, it seems that the theoretical values published thus far converge towards a value around $930\ cm^{-1}$, very close to the recent experimental result.

Apart from that, it is worth quoting three semiempirical results obtained by "morphing" the theoretical potential energy curve in order to reproduce the experimentally measured vibrational levels [44]. These values are 933.0, 933.2, and $934.6\ cm^{-1}$. It is difficult to estimate the error of these values but we feel that these semiempirical results are also consistent with our final value, $929.0 \pm 1.9\ cm^{-1}$.

V. CONCLUSIONS AND OUTLOOK

We have obtained a reliable value of the interaction energy for the beryllium dimer by using STO basis sets combined with high-level quantum chemistry methods. The total error estimated by us, $1.9\ cm^{-1}$, is an order of magnitude smaller than in the previous theoretical works. The most striking advantages of STOs, as compared with GTOs, are the reliability in estimation of the core-core and core-valence correlation effects, very solid quality of extrapolations towards CBS, and improved performance in calculation of the one-electron relativistic effects. It is clear that all of these features are essential for a spectroscopically accurate determination of the potential energy curves for diatomic systems. We have not found a situation when STOs perform worse than GTO basis sets of the same size, at least among those available to us. Despite the fact that the evaluation of the two-electron integrals in the STO basis is much more computationally intensive than in the case of GTOs, we have never found it to be a practical bottleneck. An obvious disadvantage of STOs is the fact that two-electron, two-center integrals which are required for calculation of the Breit α^2 relativistic correction are very difficult to compute and we needed to resort to GTOs to compute them.

It is also worth considering the direction of further advancements which can be taken. Let us recall the fact that the ground state of the beryllium dimer is a very pathological and difficult system, e.g., the triple excitations are responsible for the bonding effects. In many different spectroscopically interesting diatomic systems the situation is not that difficult and the doubly excited determinants give the dominant contribution to the interaction energy. In such situations the explicitly correlated calculations [99,100] are an option, allowing for a much better saturation at the MP2, CCD, or CCSD levels of theory. The F12 theory of explicitly correlated calculations is now well established [101] but to apply STOs in such computations several issues of both technical and theoretical nature need to be resolved. For instance, for GTO calculations the exponential correlation factor of Ten-no [102,103] is nowadays routinely used. In the case of STO basis sets this choice is not feasible at present, due to an extremely complicated theory of evaluation of the resulting molecular two-electron integrals [104,105]. Therefore, a different correlation factor has to be adapted. Other problems such as quality and design of the auxiliary basis sets [106,107] for the resolution of identity approximation also need to be addressed. Nonetheless, the work on combining STO basis sets with explicitly correlated theories is in progress in our laboratory.

Let us suppose that the accuracy of calculation of the Born-Oppenheimer potential energy curves can be further improved by an order of magnitude, say, due to use of the explicitly correlated methods and other theoretical advancements. The dominant error would then come from

inaccuracies in calculation of the relativistic effects, especially for heavier systems. If a perturbation theory, using the Breit-Pauli Hamiltonian, can be still applied then it is natural that two-electron relativistic effects should be calculated within the STO basis sets. Therefore, sooner or later we shall face the problem of evaluation of the matrix elements of the orbit-orbit and spin-orbit operators with the exponential functions. For heavy atoms, where the perturbation theory breaks down, different approaches need to be considered, such as Douglas-Kroll-Hess transformations [108–111] or use of effective core potentials [112,113]. Neither of the above methods can straightforwardly be combined with the STO basis sets. Nonetheless, our preliminary studies showed that extensions in these directions are feasible.

We can conclude by noting that the present series of papers opens up a possibility for a significant increase of accuracy which can be routinely reached for the diatomic systems with *ab initio* methods.

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I. SUPPLEMENTAL MATERIAL FOR PAPER III

TABLE I. Composition of STO basis sets for the beryllium atom. ETCC-2 basis sets contains all functions from the first column. TC-ETCC-2 basis set contains additionally functions from the second column and ATC-ETCC-2 functions from the third column. A-ETCC-2 contains functions from the first and third columns. The symbol [k] denotes the powers of 10, 10^k.

atomic valence		tight core		diffuse	
1S	8.12906491[−01]	1S	1.17156475[+01]	1S	7.16639837[−01]
1S	1.15567845[+00]	2P	5.29709026[+00]	2P	1.05907592[+00]
1S	1.64298439[+00]			3D	1.16078021[+00]
1S	2.33576885[+00]				
1S	3.32067433[+00]				
1S	4.72087725[+00]				
1S	6.71149285[+00]				
2P	1.25956795[+00]				
2P	1.34363972[+00]				
3D	1.22675519[+00]				

TABLE II. Composition of STO basis sets for the beryllium atom. ETCC-3 basis sets contains all functions from the first column. TC-ETCC-3 basis set contains additionally functions from the second column and ATC-ETCC-3 functions from the third column. A-ETCC-3 contains functions from the first and third columns. The symbol [k] denotes the powers of 10, 10^k.

atomic valence		tight core		diffuse	
1S	8.07003147[−01]	1S	1.54935930[+01]	1S	5.78796614[−01]
1S	1.17156475[+00]	1S	2.05467840[+01]	2P	1.01069074[+00]
1S	1.70081613[+00]	2P	6.63663083[+00]	3D	1.13131315[+00]
1S	2.46915546[+00]	2P	7.90324352[+00]	4F	1.09034661[+00]
1S	3.58459012[+00]	3D	7.77891287[+00]		
1S	5.20391953[+00]				
1S	7.55477686[+00]				
1S	1.09676280[+00]				
2P	1.07328789[+00]				
2P	1.77687814[+00]				
2P	2.94170463[+00]				
3D	1.30383348[+00]				
3D	2.13842350[+00]				
4F	1.64010475[+00]				

TABLE III. Composition of STO basis sets for the beryllium atom. ETCC-4 basis sets contains all functions from the first column. TC-ETCC-4 basis set contains additionally functions from the second column and ATC-ETCC-4 functions from the third column. A-ETCC-4 contains functions from the first and third columns. The symbol [k] denotes the powers of 10, 10^k.

atomic valence		tight core		diffuse	
1S	5.56501242[−01]	1S	1.42014407[+01]	1S	4.33207693[−01]
1S	8.08302238[−01]	1S	1.82716996[+01]	2P	6.71390454[−01]
1S	1.17403603[+00]	2P	7.37173108[+00]	3D	7.58415000[−01]
1S	1.70525397[+00]	2P	9.86210540[+00]	4F	8.96307000[−01]
1S	2.47683292[+00]	2P	1.20127077[+01]	5G	1.02303000[+00]
1S	3.59752943[+00]	3D	8.37590965[+00]		
1S	5.22530925[+00]	3D	1.01997372[+01]		
1S	7.58961318[+00]	4F	1.03564887[+01]		
1S	1.10236975[+01]				
2P	1.05442022[+00]				
2P	1.53765795[+00]				
2P	2.24236213[+00]				
2P	3.27003019[+00]				
3D	1.64562346[+00]				
3D	2.00041535[+00]				
3D	2.43169940[+00]				
4F	1.89664325[+00]				
4F	2.36427250[+00]				
5G	2.08330750[+00]				

TABLE IV. Composition of STO basis sets for the beryllium atom. ETCC-5 basis sets contains all functions from the first column. TC-ETCC-5 basis set contains additionally functions from the second column and ATC-ETCC-5 functions from the third column. A-ETCC-5 contains functions from the first and third columns. The symbol [k] denotes the powers of 10, 10^k.

atomic valence		tight core		diffuse	
1S	5.56501242[−01]	1S	1.41661255[+01]	1S	4.33207693[−01]
1S	8.08302238[−01]	1S	1.82673049[+01]	2P	6.71390454[−01]
1S	1.17403603[+00]	2P	7.64626062[+00]	3D	7.58415000[−01]
1S	1.70525397[+00]	2P	9.32939497[+00]	4F	8.96307000[−01]
1S	2.47683292[+00]	2P	1.22141834[+01]	5G	1.02303000[+00]
1S	3.59752943[+00]	2P	1.49624822[+01]	6H	1.15254000[+00]
1S	5.22530925[+00]	3D	8.37670437[+01]		
1S	7.58961318[+00]	3D	1.08645717[+01]		
1S	1.10236975[+01]	3D	1.31895798[+01]		
2P	1.02727422[+00]	4F	1.05215329[+01]		
2P	1.37069132[+00]	4F	1.30025625[+01]		
2P	1.82891254[+00]	5G	1.30737136[+01]		
2P	2.44031682[+00]				
2P	3.25611314[+00]				
3D	1.61171171[+00]				
3D	1.99156275[+00]				
3D	2.46093774[+00]				
3D	3.04093585[+00]				
4F	1.88029525[+00]				
4F	2.35223572[+00]				
4F	2.94262984[+00]				
5G	2.07200250[+00]				
5G	2.84830932[+00]				
6H	2.28502000[+00]				

TABLE V. Composition of STO basis sets for the beryllium atom. ETCC-6 basis sets contains all functions from the first column. TC-ETCC-6 basis set contains additionally functions from the second column and ATC-ETCC-6 functions from the third column. A-ETCC-6 contains functions from the first and third columns. The symbol [k] denotes the powers of 10, 10^k.

atomic valence		tight core		diffuse	
1S	5.56783742[−01]	1S	1.41615676[+01]	1S	4.33207693[−01]
1S	8.08758496[−01]	1S	1.81731145[+01]	2P	6.71390454[−01]
1S	1.17476545[+00]	1S	2.10111090[+01]	3D	7.58415000[−01]
1S	1.70641035[+00]	2P	6.70939146[+00]	4F	8.96307000[−01]
1S	2.47865332[+00]	2P	9.58760679[+00]	5G	1.02303000[+00]
1S	3.60037799[+00]	2P	1.15480836[+01]	6H	1.15254000[+00]
1S	5.22974374[+00]	2P	1.26805311[+01]	7I	1.28205000[+00]
1S	7.59648561[+00]	2P	1.50027450[+01]		
1S	1.10343062[+01]	3D	8.24507721[+00]		
1S	1.60279264[+01]	3D	1.01353767[+01]		
2P	1.02727422[+00]	3D	1.36819059[+01]		
2P	1.37069132[+00]	3D	1.59970467[+01]		
2P	1.82891254[+00]	4F	1.01588758[+01]		
2P	2.44031682[+00]	4F	1.24513361[+01]		
2P	3.25611314[+00]	4F	1.49991098[+01]		
2P	4.34462965[+00]	5G	1.29310679[+01]		
3D	1.61171171[+00]	5G	1.49929135[+01]		
3D	1.99156275[+00]	6H	1.50083302[+01]		
3D	2.46093774[+00]				
3D	3.04093585[+00]				
3D	3.75762893[+00]				
4F	1.88029525[+00]				
4F	2.35223573[+00]				
4F	2.94262984[+00]				
4F	3.68120859[+00]				
5G	2.07200250[+00]				
5G	2.84830932[+00]				
5G	3.91547113[+00]				
6H	2.28502000[+00]				
6H	3.42753000[+00]				
7I	2.51517000[+00]				

TABLE VI. Composition of the S-extended set of orbitals which are used for the relativistic calculations. See the main text for a more detailed description. The symbol [k] denotes the powers of 10, 10^k.

orbital	exponent
1S	5.30689678[−01]
1S	7.58433830[−01]
1S	1.08391382[+00]
1S	1.54907273[+00]
1S	2.21385343[+00]
1S	3.16392312[+00]
1S	4.52171284[+00]
1S	6.46219464[+00]
1S	9.23542936[+00]
1S	1.31987909[+01]
1S	1.88630191[+01]
1S	2.69580367[+01]
1S	3.85270110[+01]
1S	5.50607817[+01]
1S	7.86899790[+01]

TABLE VII. Total energies of the beryllium dimer and atom calculated with frozen-core FCI method. E_{HF} denotes the Hartree-Fock energy, E_c denotes the correlation energy. All values are given in the atomic units.

	dimer		atom	
basis set	E_{HF}	E_c	E_{HF}	E_c
A-ETCC-2	−29.1339418	−0.1046873	−14.5730210	−0.0456697
A-ETCC-3	−29.1341621	−0.1070574	−14.5730222	−0.0459687
A-ETCC-4	−29.1341745	−0.1076392	−14.5730231	−0.0460547
A-ETCC-5	−29.1341751	−0.1078505	−14.5730231	−0.0460901
A-ETCC-6	−29.1341754	−0.1079423	−14.5730231	−0.0461091

TABLE VIII. Total energies of the beryllium dimer calculated using various methods. These data are used for determination of the inner-shell effects in the main text. All values are given in the atomic units. AE and FC are abbreviations for all-electron and frozen-core, respectively.

method	ATC-ETCC-2	ATC-ETCC-3	ATC-ETCC-4	ATC-ETCC-5
AE CCSD	−29.314113	−29.326129	−29.329407	−29.330683
FC CCSD	−29.234293	−29.236054	−29.236511	−29.236681
AE CCSDT	−29.319440	−29.332239	−29.335682	–
FC CCSDT	−29.238668	−29.240909	−29.241460	–
AE CCSD(T)	−29.318577	−29.331420	−29.334925	−29.3362862
FC CCSD(T)	−29.237825	−29.240129	−29.240743	−29.2409768
AE MP2	−29.275033	−29.290336	−29.295338	−29.297525
FC MP2	−29.200976	−29.204964	−29.206567	−29.207354
AE MP4	−29.311536	−29.323856	−29.327167	−29.328456
FC MP4	−29.230630	−29.232484	−29.232926	−29.233094

TABLE IX. Total energies of the beryllium atom calculated using various methods. These data are used for determination of the inner-shell effects in the main text. All values are given in the atomic units. AE and FC are abbreviations for all-electron and frozen-core, respectively.

method	ATC-ETCC-2	ATC-ETCC-3	ATC-ETCC-4	ATC-ETCC-5
AE CCSD	−14.658664	−14.663937	−14.665410	−14.665991
FC CCSD	−14.618818	−14.619015	−14.619088	
AE CCSDT	−14.659133	−14.664551	−14.666054	–
FC CCSDT	–	–	–	–
AE CCSD(T)	−14.659105	−14.664521	−14.666028	−14.666621
FC CCSD(T)	−14.618818	−14.619015	−14.619089	−14.619120
AE MP2	−14.637838	−14.644723	−14.646999	−14.647990
FC MP2	−14.600887	−14.602168	−14.602758	−14.603055
AE MP4	−14.655016	−14.660288	−14.661743	−14.662320
FC MP4	−14.614629	−14.614731	−14.614767	−14.614789

Paper IV

"Calculation of STOs electron repulsion integrals by ellipsoidal expansion and large-order approximations"

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Commentary

In Paper IV we expand the theory presented in Paper II and return to calculation of the integrals with the help of the Neumann expansion. As mentioned in Paper II the most troublesome aspect of the Neumann expansion is the fact it leads to infinite summations. To assure that the results are well-converged basic quantities of a considerably large order must be evaluated. This is both technically challenging and computationally inefficient. To improve the situation one can propose asymptotic formulae which approximate the higher-order terms in the expansion. With such asymptotic approximations at hand only lower-order terms in the Neumann expansion must be evaluated from the exact expressions. The remainder can be efficiently calculated from the large-order formulae. Note that typically the cost of the calculations increases quickly with the order of terms when the exact expression are used. In the case of the large-order formulae this is exactly the opposite. An additional benefit of the asymptotic expansions is the possibility of estimating how many terms in the expansion are actually needed prior to the most expensive steps of the computations. This increases the efficiency of the algorithms even further, reducing the computational overhead connected with the use of STOs.

Unfortunately, the majority of the basic quantities appearing in the Neumann expansion are expressed as integrals over the Legendre functions of the first and second kind. The large-order approximations of these functions are well-known in the literature but are cumbersome and impractical. Therefore, this direct approach is probably doomed to fail. However, very simple and convenient large-order approximations of the spherical Bessel functions have recently been reported in the literature. It turns out that the differential equations derived in Paper II can be used to establish new integral representations of the most important basic quantities. These representations are not particularly advantageous compared to the initial formulations apart from the fact that they are given solely in terms of the spherical Bessel functions. Therefore, the asymptotic expansions of the latter functions can be used to derive large-order asymptotic approximations of all basic quantities defined in Paper II.

Apart from the immediate practical advantages of the asymptotic relations they can be used for several other purposes. For instance, they provide strict analytic information on how the Neumann expansion converges to its limit. This knowledge can be used in the future, e.g. to design dedicated convergence accelerators which reduce the number of terms necessary to reach the prescribed accuracy.

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ORIGINAL PAPER

Calculation of STOs electron repulsion integrals by ellipsoidal expansion and large-order approximations

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Abstract For general two-electron two-centre integrals over Slater-type orbitals (STOs), the use of the Neumann expansion for the Coulomb interaction potential yields infinite series in terms of few basic functions. In many important cases the number of terms necessary to achieve convergence by a straightforward summation is large and one is forced to calculate the basic integrals of high order. We present a systematic approach to calculation of the higher-order terms in the Neumann series by large-order expansions of the basic integrals. The final expressions are shown to be transparent and straightforward to implement, and all auxiliary quantities can be calculated analytically. Moreover, numerical stability and computational efficiency are also discussed. Results of the present work can be used to speed up calculations of the STOs integral files, but also to study convergence of the Neumann expansion and develop appropriate convergence accelerators.

Keywords Slater-type orbitals · Two-electron integrals · Large-order expansion · Neumann series

1 Introduction

From a purely theoretical point of view, Slater-type orbitals [1,2] (STOs) constitute a more convenient basis set for calculations in quantum chemistry than the widely used Gaussian-type orbitals [3] (GTOs). In fact, unlike GTOs, STOs are able to satisfy the Kato's cusp condition [4] at the electron-nucleus coalescence points and their exponential decay at large electron-nucleus distances coincides with the asymptotic

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form of the electronic density [5] (if nonlinear parameters are suitably chosen). Only severe difficulties in calculation of the electron repulsion integrals made the use of STOs drastically limited. Nonetheless, a considerable interest remained in this field [6–27].

In recent three paper series [28–30] calculation of the STOs integrals has been reconsidered and new analytical or seminumerical methods for their computation have been proposed. This allowed to perform calculations for the beryllium dimer with STOs basis sets up to sextuple ζ quality, reaching the so-called spectroscopic accuracy (few wavenumbers, cm^{-1}). Additionally, it was found that the Coulomb, $(aa|bb)$, and hybrid, $(aa|ab)$, integrals are not troublesome and are computed with a decent accuracy and speed for a reasonable range of nonlinear parameters (and quantum numbers). Calculation of the exchange integrals, $(ab|ab)$, is more involved. The Neumann expansion of the interaction potential, which is the method of choice, gives rise to infinite series. In many important cases the required accuracy is obtained after summing 20–30 terms. However, there are situations where a larger number of terms is necessary to achieve convergence which makes calculations significantly more expensive. This is one of the major reasons for the STOs versus GTOs gap in the computational timings.

It seems reasonable to expect that the higher-order terms in the Neumann expansion do not need to be computed with general techniques but a suitable large-order expansion can be devised. This would allow to reduce the computational burden significantly, as the asymptotic expansions of such kind are typically more robust than the general expressions. Therefore, the main purpose of this paper is to derive systematic large-order approximations of all basic quantities appearing in the Neumann expansion of the STOs exchange integrals, and provide necessary numerical tests. Resulting expressions can be readily incorporated into existing STOs integral codes.

Since the present paper is concentrated solely on the Neumann expansion of the interaction potential with application to the STOs electron repulsion integrals, a brief survey of the literature on this topic is mandatory. Relevant mathematical details will be given in the next section. Possibly the first method utilising the Neumann expansion was reported by Ruedenberg [31,32] who introduced general expressions based on charge distributions of both electrons. Later, this approach was extended by applying a straightforward numerical integration [33,34] to avoid several difficult analytic rearrangements. Kotani [35] provided many tools and expressions enabling fully analytical (albeit recursive) techniques to be used. Recursive approach was later pursued by Harris [36] who invoked the theory of spherical Bessel functions to simplify the existing theory and discovered many useful additional relations. A considerable interest remained in the field despite GTOs were clearly taking over the role of routine basis set in quantum chemistry. Many changes were introduced in how individual terms in the Neumann expansion are computed. They were aimed at improving the efficiency, accuracy or generality of the algorithms; the works of Yasui and Saika [37], and Fernández Rico et al. [38–42] are notable examples. Later, Maslen and Trefry [21] utilised an approach based on the hypergeometric function which enabled to derive closed-form succinct analytical expressions for all necessary quantities. Despite those expressions were marred with numerical instabilities, it was a considerable progress at the time. Harris [22] pursued the analytical approach of Maslen and Trefry, introduced

considerable simplifications and several new expressions which allow more stable calculations of several auxiliary quantities.

This paper is organised as follows. In Sect. 2 we introduce the notation and recall relevant expressions from the previous works. In Sect. 3 we introduce the large-order asymptotic expansion for the functions L_μ and verify the main results numerically. The corresponding expansion for the functions W_μ is given in Sect. 4. Finally, in Sect. 5 we conclude our paper.

2 Preliminaries

Let us consider a diatomic molecule placed on the z axis symmetrically around the origin. Slater-type orbitals (STOs) have the following generic form

$$\chi_{nlm}(\mathbf{r};\zeta) = S_n(\zeta)\, r^{n-1}\, e^{-\zeta r}\, Y_{lm}(\theta,\phi), \tag{1}$$

where n and l are both integers such that $n > l$, (r,θ,ϕ) are the spherical coordinates of the given centre, $S_n(\zeta) = (2\zeta)^{n+1/2}/\sqrt{(2n)!}$ is the (radial) normalisation constant, and Y_{lm} are spherical harmonics in the Condon–Shortley phase convention

$$Y_{lm}(\hat{\mathbf{r}}) = \Omega_{lm}\, P_l^{|m|}(\cos\theta)\frac{e^{im\phi}}{\sqrt{2\pi}}, \tag{2}$$

where P_l^m are the (unnormalised) associated Legendre polynomials [43] and Ω_{lm} is the angular normalisation constant

$$\Omega_{lm} = i^{m-|m|}\sqrt{\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}}. \tag{3}$$

Transformation to the real spherical harmonics, which are usually more convenient in calculations, can be performed with standard relations.

Throughout the paper the electrons shall be denoted by $1, 2, \ldots$ and the nuclei by $a, b, \ldots$. All interparticle distances are shortly written as r_{pq}, e.g., the distance between the first electron and the nucleus a is simply r_{1a} etc. (an exception is the internuclear distance for which the usual convention $R := r_{ab}$ is adapted). Let us introduce the prolate ellipsoidal coordinates, (ξ_i, η_i, ϕ_i), by means of the formulae

$$\xi_i = \frac{r_{ia} + r_{ib}}{R}, \quad \eta_i = \frac{r_{ia} - r_{ib}}{R}, \tag{4}$$

where $i = 1, 2$, and ϕ_i are the corresponding azimuthal angles. The volume element becomes $d\mathbf{r}_i = \left(\frac{R}{2}\right)^3 \left(\xi_i^2 - \eta_i^2\right)\, d\xi_i\, d\eta_i\, d\phi_i$. It is well known that the product of two Slater-type orbitals can be written in a closed-from in the prolate ellipsoidal coordinate system as follows

$$\left(\frac{R}{2}\right)^3 \left(\xi_i^2 - \eta_i^2\right) \chi^*_{n_a l_a m_a}(\mathbf{r}_{ia}; \zeta_a) \chi_{n_b l_b m_b}(\mathbf{r}_{ib}; \zeta_b)$$
$$= \frac{K_{ab}}{2\pi} e^{-\alpha_i \xi_i - \beta_i \eta_i} \left[\left(\xi_i^2 - 1\right)\left(1 - \eta_i^2\right)\right]^{|M_i|/2} e^{iM_i\phi} \sum_{p,q=0}^{\Gamma} \Xi_{pq} \xi_i^p \, \eta_i^q, \quad (5)$$

with $M = m_a - m_b$ and $\Gamma = l_a + l_b + 2$. The new coefficients are defined as $\alpha = \frac{R}{2}(\zeta_a + \zeta_b)$, $\beta = \frac{R}{2}(\kappa_a \zeta_a + \kappa_b \zeta_b)$, $K_{ab} = S_{n_a}(\zeta_a) S_{n_b}(\zeta_b)\, \Omega_{l_a m_a} \Omega_{l_b m_b} \left(\frac{R}{2}\right)^{n_a + n_b + 1}$. The quantity Ξ is a square matrix with some numerical coefficients which can be tabulated. Details of this transformation are given in Refs. [29] (see also the references therein). In conclusion, any nonzero two-centre electron repulsion integral over STOs can be written down as a finite linear combination of the following generic integrals

$$\mathcal{I}^{p_2 q_2}_{p_1 q_1}(\sigma) = \int_1^\infty d\xi_1 \int_{-1}^{+1} d\eta_1 \int_0^{2\pi} d\phi_1 \int_1^\infty d\xi_2 \int_{-1}^{+1} d\eta_2 \int_0^{2\pi} d\phi_2 \, \xi_1^{p_1} \eta_1^{q_1} \xi_2^{p_2} \eta_2^{q_2}$$
$$\times e^{-\alpha_1 \xi_1 - \alpha_2 \xi_2 - \beta_1 \eta_1 - \beta_2 \eta_2} \left[\left(\xi_1^2 - 1\right)\left(1 - \eta_1^2\right)\left(\xi_2^2 - 1\right)\left(1 - \eta_2^2\right)\right]^{\sigma/2} \frac{1}{r_{12}}, \quad (6)$$

where explicit notation for the nonlinear parameters has been suppressed for brevity. The values of p_i, q_i and σ are restricted to non-negative integers.

Let us now introduce the Neumann expansion of the Coulomb interaction potential

$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{\mu=0}^{\infty} \sum_{\sigma=-\mu}^{\mu} (-1)^\sigma (2\mu + 1) \left[\frac{(\mu - |\sigma|)!}{(\mu + |\sigma|)!}\right]^2$$
$$\times \; P_\mu^{|\sigma|}(\xi_<) Q_\mu^{|\sigma|}(\xi_>) P_\mu^{|\sigma|}(\eta_1) P_\mu^{|\sigma|}(\eta_2) e^{i\sigma(\phi_1 - \phi_2)}, \quad (7)$$

where $\xi_< = \min(\xi_1, \xi_2)$ and $\xi_> = \max(\xi_1, \xi_2)$, P_l^m are defined in the same way as in Eq. (2), and Q_l^m are the associated Legendre functions of the second kind. By plugging the above expansion into Eq. (6) and after a straightforward integration over the angles one arrives at

$$\mathcal{I}^{p_2 q_2}_{p_1 q_1}(\sigma) = \frac{8}{R}(-1)^\sigma \sum_{\mu=\sigma}^{\infty} (2\mu + 1) W^\sigma_\mu(p_1, p_2, \alpha_1, \alpha_2) i^\sigma_\mu(q_1, \beta_1) i^\sigma_\mu(q_2, \beta_2), \quad (8)$$

where the basic quantities for the integration over η are

$$i^\sigma_\mu(q, \beta) = \frac{(-1)^\mu}{2} \frac{(\mu - \sigma)!}{(\mu + \sigma)!} \int_{-1}^{+1} d\eta \, P_\mu^{|\sigma|}(\eta)(1 - \eta^2)^{\sigma/2} \eta^q \, e^{-\beta\eta}, \quad (9)$$

and similarly for the ξ integration

$$W^\sigma_\mu(p_1, p_2, \alpha_1, \alpha_2) = w^\sigma_\mu(p_1, p_2, \alpha_1, \alpha_2) + w^\sigma_\mu(p_2, p_1, \alpha_2, \alpha_1), \quad (10)$$

$$w_\mu^\sigma(p_1, p_2, \alpha_1, \alpha_2) = \int_1^\infty d\xi_1\, Q_\mu^\sigma(\xi_1) \left(\xi_1^2 - 1\right)^{\sigma/2} \xi_1^{p_1} e^{-\alpha_1 \xi_1} \times \int_1^{\xi_1} d\xi_2\, P_\mu^\sigma(\xi_2) \left(\xi_2^2 - 1\right)^{\sigma/2} \xi_2^{p_2} e^{-\alpha_2 \xi_2}. \quad (11)$$

In general, the expansion given by Eq. (8) is infinite and terminates only in the special case of vanishing β_1 or β_2. Nonetheless, it is convergent for any physically acceptable values of the nonlinear parameters, i.e., $\alpha_i > 0$ and $|\beta_i| \leq \alpha_i$, but the *rate* of convergence depends crucially on the values of β_i. A practical observation is that larger values of β_i result in a slower convergence. Unfortunately, in actual calculations one can expect some of the integrals to approach the extreme case $|\beta_i| = \alpha_i$. In such situation several tens of terms may be necessary to achieve convergence which significantly slows down the computations. Note parenthetically that the convergence is somewhat slower for larger values of σ, but this effect is of secondary importance.

Calculation of the integrals $i_\mu^\sigma(q, \beta)$ is not connected with any significant overhead, even if large values of the parameters are necessary. Therefore, at present we see no reason to develop new methods for their computation. The available techniques appear to be entirely satisfactory and the recursive method put forward by Harris is particularly robust (see Ref. [22] for an extended survey). We shall concentrate on the most difficult basic quantities, i.e., the integrals $w_\mu^\sigma(p_1, p_2, \alpha_1, \alpha_2)$. Let us recall the analytical formula derived by Maslen and Trefry (after simplifications due to Harris)

$$w_\mu^\sigma(p_1, p_2, \alpha_1, \alpha_2) = \left[\frac{(\mu+\sigma)!}{(\mu-\sigma)!}\right]^2 \left[L_\mu^\sigma(p_1, \alpha_1) k_\mu^\sigma(p_2, \alpha_2) - \sum_s^\mu \mathcal{A}_s^{\mu\sigma} \sum_{j=0}^{p_2+s} \frac{(p_2+s)!}{j!\alpha_2^{p_2+s}} L_\mu^\sigma(p_1+j, \alpha_1+\alpha_2)\right], \quad (12)$$

where

$$L_\mu^\sigma(p, \alpha) = \frac{(\mu-\sigma)!}{(\mu+\sigma)!} \int_1^\infty d\xi\, Q_\mu^\sigma(\xi) \xi^p (\xi^2-1)^{\sigma/2} e^{-\alpha\xi}, \quad (13)$$

and

$$k_\mu^\sigma(p, \alpha) = \frac{(\mu-\sigma)!}{(\mu+\sigma)!} \int_1^\infty d\xi\, P_\mu^\sigma(\xi) \xi^p (\xi^2-1)^{\sigma/2} e^{-\alpha\xi}. \quad (14)$$

The main goal of the present paper is to provide efficient and reliable methods for calculation of W_μ for large values of μ. The problem can be solved in two ways. The first one is a direct attack by using the differential equation for W_μ derived in the previous paper. The second method utilises Eq. (12) and reduces the problem to calculation of $L_\mu^\sigma(p, \alpha)$ which appears to be more straightforward. In fact, large μ expansion of $L_\mu^\sigma(p, \alpha)$ is expected to be significantly less complicated than the corresponding one for W_μ. However, there is an additional cost of using Eq. (12) which is absent in the first method where W_μ are calculated directly. Let us also note

in passing that the auxiliary integrals $k_\mu^\sigma(p,\alpha)$, Eq. (14), can be computed efficiently with the available techniques and thus are not considered herein.

Throughout the paper we rely on two special functions, $E_n(z)$ and $a_n(z)$. They are defined in the "Appendix 1" and efficient methods of their computation are briefly discussed.

3 Large-order expansion of $L_\mu^\sigma(p;\alpha)$

3.1 Initial reduction

Let us recall two recursion relations which allow to simplify the problem significantly. They result directly from the properties of the Legendre functions and read

$$L_\mu^0(p+1,\alpha) = \frac{(\mu+1)L_{\mu+1}^0(p,\alpha) + \mu L_{\mu-1}^0(p,\alpha)}{2\mu+1}, \tag{15}$$

$$L_\mu^{\sigma+1}(p,\alpha) = \frac{L_{\mu+1}^\sigma(p,\alpha) - L_{\mu-1}^\sigma(p,\alpha)}{2\mu+1}. \tag{16}$$

By means of these recursions the necessary integrals $L_\mu^\sigma(p;\alpha)$ can be efficiently computed starting with $L_\mu(\alpha) := L_\mu^0(0;\alpha)$ only. Note that the above expressions require $L_\mu(\alpha)$ with even larger μ than initially. In fact, they basically consist of increasing p and σ at cost of μ. Therefore, the most important task is to calculate the integrals $L_\mu(\alpha)$ for large μ with decent speed and precision. This is the main issue considered in the present section.

3.2 Alternative integral representations of $L_\mu(\alpha)$

Our derivation starts with the differential equation for $L_\mu(\alpha)$ which was established in Ref. [29]

$$\alpha^2 L_\mu''(\alpha) + 2\alpha L_\mu'(\alpha) - \left[\mu(\mu+1) + \alpha^2\right] L_\mu(\alpha) = -e^{-\alpha}, \tag{17}$$

where the prime denotes differentiation with respect to α. Let us recall that the linearly independent solutions of the homogeneous differential equation are the well-known modified spherical Bessel functions [43], $i_\mu(\alpha)$ and $k_\mu(\alpha)$. This suggests that the desired solution of the inhomogeneous equation has the following form

$$\mathcal{K}_\mu(\alpha)\, i_\mu(\alpha) + \mathcal{I}_\mu(\alpha)\, k_\mu(\alpha), \tag{18}$$

where $\mathcal{I}_\mu(\alpha)$ and $\mathcal{K}_\mu(\alpha)$ are some functions which are yet to be determined. Let us additionally enforce the constraint

$$\mathcal{K}_\mu'(\alpha)\, i_\mu(\alpha) + \mathcal{I}_\mu'(\alpha)\, k_\mu(\alpha) = 0, \tag{19}$$

valid strictly for every value of $\alpha > 0$. Upon inserting the formula (18) into the differential equation (17) one obtains the following expression

$$\mathcal{K}'_\mu(\alpha)\, i'_\mu(\alpha) + \mathcal{I}'_\mu(\alpha)\, k'_\mu(\alpha) = -\frac{e^{-\alpha}}{\alpha^2}, \tag{20}$$

where we have taken advantage of the fact that $i_\mu(\alpha)$ and $k_\mu(\alpha)$ obey the homogeneous differential equation. The above expression and the constraint (19) form the following system of linear equations

$$\begin{bmatrix} i_\mu(\alpha) & k_\mu(\alpha) \\ i'_\mu(\alpha) & k'_\mu(\alpha) \end{bmatrix} \begin{bmatrix} \mathcal{K}'_\mu(\alpha) \\ \mathcal{I}'_\mu(\alpha) \end{bmatrix} = \begin{bmatrix} -e^{-\alpha}/\alpha^2 \\ 0 \end{bmatrix} \tag{21}$$

Note that the determinant of the above 2×2 matrix (the Wronskian) is equal to $-\frac{\pi}{2}\frac{1}{\alpha^2}$ which is a direct consequence of the properties of the Bessel functions [43]. The system of linear equations (21) can be solved right away, e.g., with the Cramer's rule to give

$$\mathcal{K}'_\mu(\alpha) = +\frac{2}{\pi}\, e^{-\alpha}\, k_\mu(\alpha), \tag{22}$$

$$\mathcal{I}'_\mu(\alpha) = -\frac{2}{\pi}\, e^{-\alpha}\, i_\mu(\alpha), \tag{23}$$

and after (indefinite) integration over α one arrives at

$$\frac{2}{\pi}\, i_\mu(\alpha) \int d\alpha\, e^{-\alpha}\, k_\mu(\alpha) - \frac{2}{\pi}\, k_\mu(\alpha) \int d\alpha\, e^{-\alpha}\, i_\mu(\alpha). \tag{24}$$

This expression is the general solution of the differential equation (17). In order to find a particular solution corresponding to the integrals (13) we need to impose proper initial conditions. From Eq. (17) one clearly sees that $L_\mu(\alpha)$ vanish as $\alpha \to \infty$ for every μ. Additionally, the results presented in Ref. [29] indicate that $L_\mu(\alpha)$ vanish exponentially quickly in this limit [as $e^{-\alpha}\log(\alpha)$ in the leading-order term]. This constitutes the first initial condition which we need to impose on the above general solution. The second initial condition results from the small α behaviour of $L_\mu(\alpha)$

$$L^0_\mu(\mu, \alpha) = -\gamma_E \frac{\mu!}{(2\mu+1)!!} - \frac{\mu!}{(2\mu+1)!!} \log(2\alpha) + \widetilde{\mathcal{M}}_\mu + \mathcal{O}(\alpha), \tag{25}$$

where γ_E is the Euler–Mascheroni constant, and $\widetilde{\mathcal{M}}_\mu$ are some numerical coefficients independent of α (c.f. the supplemental material to Ref. [29]). An essential feature of the above formula is the logarithmic singularity for small α which has to be reproduced by Eq. (24). The most succinct formula which takes both initial conditions into account reads

$$L_\mu(\alpha) = \mathcal{K}_\mu(\alpha)\, i_\mu(\alpha) + \mathcal{I}_\mu(\alpha)\, k_\mu(\alpha), \tag{26}$$

$$\mathcal{K}_\mu(\alpha) = \frac{2}{\pi}\int_\alpha^\infty dz\, e^{-z}\, k_\mu(z), \tag{27}$$

$$\mathcal{I}_\mu(\alpha) = \frac{2}{\pi}\int_0^\alpha dz\, e^{-z}\, i_\mu(z). \tag{28}$$

Clearly, the formula (26) is a new integral representation of the $L_\mu(\alpha)$ functions, alternative to the definition given by Eq. (13).

At this point an extended comment is mandatory. One might be uncertain about the reason behind introduction of Eq. (26). It is clearly more complicated than the initial definition, Eq. (13), and appears to give no computational or theoretical advantages. However, it turns out that Eq. (13) is a very inconvenient starting point for the present developments. Despite the large-order expansions of the Legendre functions, Q_μ, are well-known [44–46], they are too complicated to be used for our purposes. A naive approach where a large-order expansion of Q_μ is inserted into Eq. (13) leads to intractable integrals requiring a numerical solution. On the other hand, Eq. (26) is formulated solely in terms of the modified spherical Bessel functions. This is advantageous, as the large-order expansions of $i_\mu(\alpha)$ and $k_\mu(\alpha)$ are more compact and straightforward. In particular, we rely on the recent works of Sidi and Hoggan [47,48] where an elegant formulation has been given. For convenience of the readers we list the relevant formulae of Sidi and Hoggan in the "Appendix 2", utilising our notation.

3.3 Large-order expansion of $L_\mu(\alpha)$

Having the integral representation (26) at hand, it becomes straightforward to derive the large-order expansion of the pertinent integrals $\mathcal{I}_\mu(\alpha)$ and $\mathcal{K}_\mu(\alpha)$. By inserting the integral representations (68) and (69) into Eqs. (27) and (28), respectively, one obtains

$$\mathcal{I}_\mu(\alpha) = \frac{2}{\sqrt{\pi}}\left(\frac{\alpha}{2}\right)^{\mu+1}\frac{1}{\Gamma(\mu+3/2)}\sum_{m=0}^\infty \frac{\lambda_m^\mu(\alpha)}{(\mu+1/2)^m}, \tag{29}$$

$$\mathcal{K}_\mu(\alpha) = \frac{1}{\sqrt{\pi}}\left(\frac{2}{\alpha}\right)^{\mu}\Gamma(\mu+1/2)\sum_{m=0}^\infty \frac{\Lambda_m^\mu(\alpha)}{(\mu+1/2)^m}(-1)^m, \tag{30}$$

after a simple exchange of variables. The coefficients in the expansions are obtained with help of Eq. (70)

$$\lambda_m^\mu(\alpha) = \int_0^1 dt\, t^\mu\, b_m(\alpha t)\, e^{-\alpha t} = \sum_{k=1}^m (-1)^{m-k}\frac{S_{mk}}{k!}(\alpha/2)^{2k} a_{\mu+2k}(\alpha), \tag{31}$$

$$\Lambda_m^\mu(\alpha) = \int_1^\infty dt\, \frac{b_m(\alpha t)}{t^{\mu+1}}\, e^{-\alpha t} = \sum_{k=1}^m (-1)^{m-k}\frac{S_{mk}}{k!}(\alpha/2)^{2k} E_{\mu-2k-1}(\alpha), \tag{32}$$

which is valid for $m > 0$. In the special case of $m = 0$ the corresponding results are $\lambda_0^\mu(\alpha) = a_\mu(\alpha)$ and $\Lambda_0^\mu(\alpha) = E_{\mu+1}(\alpha)$. The modified spherical Bessel functions in Eq. (26) which multiply the integrals $\mathcal{I}_\mu(\alpha)$ and $\mathcal{K}_\mu(\alpha)$ can also be expanded with

help of Eqs. (68) and (69). This leads to a product of two infinite series which can finally be rewritten as

$$L_\mu(\alpha) = \frac{1}{2\mu+1} \sum_{s=0}^{\infty} \frac{c_s^\mu(\alpha)}{(\mu+1/2)^s}, \tag{33}$$

$$c_s^\mu(\alpha) = \sum_{l=0}^{s} b_{s-l}(\alpha)(-1)^l \Big[\Lambda_l^\mu(\alpha) + (-1)^s \lambda_l^\mu(\alpha) \Big]. \tag{34}$$

A short remark on the mathematical nature of the above expansion is necessary. Note that Eq. (33) would not be classified as an asymptotic expansion by some authors because the coefficients c_s^μ are explicitly μ-dependent. That is why we prefer to use the term large-order expansion. We verified that Eq. (33) is capable of providing arbitrarily accurate results if only the value of μ is sufficiently large. Thus, from the pragmatic point of view, Eq. (33) gives an effective method to calculate the values of $L_\mu(\alpha)$ for large μ where other techniques run out of steam.

From the point of view of some developments it is useful to analyse in details the first term of the expansion (33). One easily arrives at

$$L_\mu(\alpha) = \frac{1}{2\mu+1} \big[E_{\mu+1}(\alpha) + a_\mu(\alpha) \big] + \text{h.o.} \tag{35}$$

Additionally, if the large μ asymptotic formulae for $E_{\mu+1}(\alpha)$ and $a_\mu(\alpha)$ are used, Eqs. (66) and (67), some simplifications occur and one finds

$$L_\mu(\alpha) = \frac{e^{-\alpha}}{2\mu+1} \left[\frac{1}{\mu-\alpha} + \frac{1}{\mu+\alpha} \right] + \mathcal{O}\left(\frac{1}{\mu^3} \right), \tag{36}$$

provided that $\mu > \alpha$.

3.4 Numerical tests and examples

It is now mandatory to verify how the new formula (33) works in practice. In Table 1 we present results of some exemplary calculations of $L_\mu(\alpha)$ with help of the new formula, Eq. (33). Different values of α and μ are tested to find the actual range of applicability. Additionally, the number of terms in the infinite expansion (33) necessary to reach the maximal possible precision was listed in each case. A more detailed inspection of Table 1 reveals some general conclusions about the range of the parameters where Eq. (33) gives sufficiently accurate results. One sees that the convergence of the infinite summation in Eq. (33) is excellent for small or moderate values of α. Unfortunately, it deteriorates quickly when the values of α and μ approach each other. In the case when $\alpha > \mu$ no useful information about $L_\mu(\alpha)$ can be obtained with help of Eq. (33). However, this is not a reason for a major concern. In fact, the large α expansion of $L_\mu(\alpha)$ was given in Ref. [29] and it works reasonably well for both small and large values of μ. We conclude that Eq. (33) is a preferred computational technique when μ is large and α is small or moderate at the same time.

Table 1 The functions $L_\mu(\alpha)$ calculated for some representative values of α and μ

μ	Exact	Large-order expansion	Convergence
$\alpha = 0.1$			
30	9.72 733 864 877 071 [−04]	9.72 733 864 877 071 [−04]	9
40	5.51 662 783 117 224 [−04]	5.51 662 783 117 224 [−04]	9
50	3.54 810 355 237 372 [−04]	3.54 810 355 237 372 [−04]	7
60	2.47 209 822 882 328 [−04]	2.47 209 822 882 328 [−04]	7
$\alpha = 1.0$			
30	3.94 720 438 208 518 [−04]	3.94 720 438 208 518 [−04]	13
40	2.24 043 509 438 319 [−04]	2.24 043 509 438 319 [−04]	11
50	1.44 153 386 177 520 [−04]	1.44 153 386 177 520 [−04]	9
60	1.00 458 613 132 488 [−04]	1.00 458 613 132 488 [−04]	9
$\alpha = 10.0$			
30	4.78 078 398 572 794 [−08]	4.78 078 398 572 794 [−08]	29
40	2.73 528 592 642 051 [−08]	2.73 528 592 642 051 [−08]	21
50	1.76 662 929 639 839 [−08]	1.76 662 929 639 839 [−08]	19
60	1.23 372 624 613 915 [−08]	1.23 372 624 613 915 [−08]	19
$\alpha = 30.0$			
30	9.48 264 212 820 654 [−17]	Divergence	–
40	5.51 072 668 384 366 [−17]	Divergence	–
50	3.58 705 498 786 413 [−17]	3.58 705 498 786 412 [−17]	51
60	2.51 610 451 657 133 [−17]	2.51 610 451 657 133 [−17]	41

Exact denotes values calculated using explicit expressions (c.f. Ref. [29]) in extended arithmetic precision with the MATHEMATICA package (all digits shown are correct). *Large-order expansion* column shows results of calculations with Eq. (47) in the double precision arithmetic. *Convergence* denotes a number of terms in Eq. (47) required to converge the summation to relative precision of 2×10^{-16}. The symbol $[k]$ denotes the powers of 10, 10^k

4 Large-order expansion of $W_\mu^\sigma(p_1, p_2; \alpha_1, \alpha_2)$

4.1 Initial reduction

Let us reduce the number of independent parameters in the integrals W_μ by using two convenient formulae. The first one is the remainder in the recursive method proposed by Kotani [35]

$$\begin{aligned} W_\mu^{\sigma+1}(p_1, p_2, \alpha_1, \alpha_2) &= \frac{(\mu-\sigma)(\mu-\sigma+1)^2}{2\mu+1} W_{\mu+1}^\sigma(p_1, p_2, \alpha_1, \alpha_2) - (\mu-\sigma)(\mu+\sigma+1) \\ &\quad \times W_\mu^\sigma(p_1+1, p_2+1, \alpha_1, \alpha_2) + \frac{(\mu+\sigma+1)(\mu+\sigma)^2}{2\mu+1} W_{\mu-1}^\sigma(p_1, p_2, \alpha_1, \alpha_2). \end{aligned} \tag{37}$$

This expression is numerically stable for a wide range of the parameters values. As a result, it constitutes a reliable method for computation of $W_\mu^\sigma(p_1, p_2, \alpha_1, \alpha_2)$ from the integrals with $\sigma = 0$. Additionally, the values of p_2 can be increased by differentiation

$$W_\mu^0(p_1, p_2, \alpha_1, \alpha_2) = (-1)^{p_2} \frac{\partial^{p_2}}{\partial \alpha_2^{p_2}} W_\mu^0(p_1, 0, \alpha_1, \alpha_2). \tag{38}$$

Further in the article, we consider the large μ expansion of the basic integrals $W_\mu^0(p_1, 0, \alpha_1, \alpha_2)$. Note that differentiation with respect to α_1 could be used to increase the value of p_1, but this approach is not particularly advantageous in the present context. For convenience, we introduce the following shorthand notation, $W_\mu(p; \alpha_1, \alpha_2) = W_\mu^0(p, 0, \alpha_1, \alpha_2)$.

4.2 Alternative integral representations of $W_\mu^0(p_1, 0, \alpha_1, \alpha_2)$

Let us recall the differential equation for $W_\mu(p; \alpha_1, \alpha_2)$ obtained in Ref. [29]

$$\begin{aligned} &\alpha_2^2 \frac{\partial^2}{\partial \alpha_2^2} W_\mu(p; \alpha_1, \alpha_2) + 2\alpha_2 \frac{\partial}{\partial \alpha_2} W_\mu(p; \alpha_1, \alpha_2) + \\ &\quad - \left[\mu(\mu+1) + \alpha_2^2\right] W_\mu(p; \alpha_1, \alpha_2) = -E_{-p}(\alpha_1 + \alpha_2), \end{aligned} \tag{39}$$

which provides the starting point for our derivation. Note that the solutions of the homogeneous equation are well-known and are the same as for Eq. (17). Therefore, the solution can be written in the form analogous to Eq. (18) and the derivation follows along a very similar line as for L_μ. There is no need to repeat details of the derivation and we present only the final result

$$\begin{aligned} W_\mu(p; \alpha_1, \alpha_2) &= \mathcal{K}_\mu(p; \alpha_1, \alpha_2)\, i_\mu(\alpha_2) + \mathcal{I}_\mu(p; \alpha_1, \alpha_2)\, k_\mu(\alpha_2), \\ \mathcal{K}_\mu(p; \alpha_1, \alpha_2) &= \frac{2}{\pi} \int_{\alpha_2}^{\infty} dz\, k_\mu(z)\, E_{-p}(\alpha_1 + z), \\ \mathcal{I}_\mu(p; \alpha_1, \alpha_2) &= \frac{2}{\pi} \int_{0}^{\alpha_2} dz\, i_\mu(z)\, E_{-p}(\alpha_1 + z), \end{aligned} \tag{40}$$

by imposing proper initial conditions (c.f. Ref. [29]). Note that the basic integrals were expressed though the modified spherical Bessel functions, in analogy with L_μ functions considered before. Clearly, Eq. (40) may be useful on their own (e.g. evaluation by a numerical integration), but in the present paper we concentrate solely on the large μ expansion of $W_\mu(p; \alpha_1, \alpha_2)$.

4.3 Large-order expansion of $W_\mu^0(p_1, 0, \alpha_1, \alpha_2)$

Let us now insert the asymptotic expansions of $i_\mu(\alpha)$ and $k_\mu(\alpha)$, Eqs. (68) and (69), into the integral representation (40). After straightforward rearrangements one arrives at

$$\mathcal{I}_\mu(p;\alpha_1,\alpha_2) = \frac{2}{\sqrt{\pi}}\left(\frac{\alpha_2}{2}\right)^{\mu+1}\frac{1}{\Gamma(\mu+3/2)}\sum_{m=0}^{\infty}\frac{\tau_m^{\mu p}(\alpha_1,\alpha_2)}{(\mu+1/2)^m}, \tag{41}$$

$$\mathcal{K}_\mu(p;\alpha_1,\alpha_2) = \frac{1}{\sqrt{\pi}}\left(\frac{2}{\alpha_2}\right)^{\mu}\Gamma(\mu+1/2)\sum_{m=0}^{\infty}\frac{T_m^{\mu p}(\alpha_1,\alpha_2)}{(\mu+1/2)^m}(-1)^m, \tag{42}$$

which is an analogue of Eqs. (29). The analytical formulae for the coefficients are obtained by recalling Eq. (70)

$$\begin{aligned}\tau_m^{\mu p}(\alpha_1,\alpha_2) &= \int_0^1 dt\, t^\mu\, b_m(\alpha_2 t)\, E_{-p}(\alpha_1+\alpha_2 t)\\ &= \sum_{k=1}^{m}(-1)^{m-k}\frac{S_{mk}}{k!}(\alpha_2/2)^{2k}\,\omega_{\mu+2k,p}(\alpha_1,\alpha_2),\end{aligned} \tag{43}$$

$$\begin{aligned}T_m^{\mu p}(\alpha_1,\alpha_2) &= \int_1^\infty dt\,\frac{b_m(\alpha t)}{t^{\mu+1}}\,E_{-p}(\alpha_1+\alpha_2 t)\\ &= \sum_{k=1}^{m}(-1)^{m-k}\frac{S_{mk}}{k!}(\alpha_2/2)^{2k}\,\Omega_{2k-\mu-1,p}(\alpha_1,\alpha_2),\end{aligned} \tag{44}$$

for $m > 1$, and $\tau_m^{\mu p}(\alpha_1,\alpha_2) = \omega_{\mu p}(\alpha_1,\alpha_2)$, $T_m^{\mu p}(\alpha_1,\alpha_2) = \Omega_{-\mu-1,p}(\alpha_1,\alpha_2)$. The basic integrals are defined as

$$\omega_{np}(\alpha_1,\alpha_2) = \int_0^1 dt\, t^n E_{-p}(\alpha_1+\alpha_2 t), \tag{45}$$

$$\Omega_{np}(\alpha_1,\alpha_2) = \int_1^\infty dt\, t^n E_{-p}(\alpha_1+\alpha_2 t). \tag{46}$$

Note that evaluation of Eqs. (43) and (44) requires ω_{np} with $n > 0$, $p > 0$, but in the case of Ω_{np} the values of n can be negative. Additionally, the first argument (n) in ω_{np} is always larger than μ [c.f. Eq. (43)]. The present method is intended to be used for large μ and we concentrate on evaluation of ω_{np} with large n. Unfortunately, for the integrals Ω_{np} such simplifications do not occur and more general methods are required. Calculation of the basic integrals is discussed in the next section, with a considerable emphasis on the numerical stability.

Finally, one combines the asymptotic expansions (41) with the initial formula, Eq. (40), and after some rearrangements the following expression is obtained

$$W_\mu(p;\alpha_1,\alpha_2) = \frac{1}{2\mu+1}\sum_{s=0}^{\infty}\frac{d_s^{\mu p}}{(\mu+1/2)^s}, \tag{47}$$

where we have suppressed the notation for the nonlinear parameters, and

$$d_s^{\mu p} = \sum_{l=0}^{s} b_{s-l}(\alpha_2)(-1)^l \Big[T_l^{\mu p}(\alpha_1, \alpha_2) + (-1)^s \tau_l^{\mu p}(\alpha_1, \alpha_2) \Big], \tag{48}$$

which constitutes the main result of the present section.

4.4 Calculation of the basic integrals

Let us begin with calculation of the integrals ω_{np}. Integration of Eq. (45) by parts leads to the following recursion

$$\omega_{np}(\alpha_1, \alpha_2) = \frac{1}{n+1} E_{-p}(\alpha_1 + \alpha_2) + \frac{\alpha_2}{n+1} \omega_{n+1,p+1}(\alpha_1 + \alpha_2 t). \tag{49}$$

In principle, the above relation can be used to calculate the values of ω_{np} by downward recursion, starting at some large n with an arbitrary value. However, the main drawbacks of this approach are difficulties in controlling the error and choice of the starting point. Therefore, we propose to iterate this recursion analytically N times which gives

$$\omega_{np}(\alpha_1, \alpha_2) = n! \sum_{k=0}^{N} \frac{\alpha_2^k}{(n+k+1)!} E_{-p-k}(\alpha_1 + \alpha_2) + R_N, \tag{50}$$

$$R_N = \omega_{n+N+1,p+N+1}(\alpha_1, \alpha_2). \tag{51}$$

Note that the above expression is formally exact for each N. Additionally, when n is large the terms in the above sum vanish very quickly and large values of N give very small contributions to the total value of the integral. Similarly, the remainder R_N vanishes fast with increasing N. To estimate in advance the required values of N we establish approximate upper bounds for the values of R_N (note that R_N is positive by definition). Let us first insert the integral representation of E_{-p}, Eq. (61), into Eq. (45) and reverse the order of integrations. One arrives at the alternative integral representation of the remainder

$$R_N = \int_1^\infty dz\, z^{p+N+1} e^{-\alpha_1 z} \int_0^1 dt\, t^{n+N+1} e^{-\alpha_2 t z}, \tag{52}$$

which is strictly bounded from above by

$$R_N \le \int_1^\infty dz\, z^{p+N+1} e^{-\alpha_1 z} \int_0^1 dt\, t^{n+N+1} = \frac{1}{n+N+2} E_{-p-N-1}(\alpha_1). \tag{53}$$

Additionally, one can verify that $E_{-p-N-1}(\alpha_1)$ is bounded from above by $(p+N+1)!/\alpha_1^{p+N+1}$. This finally gives the estimation

$$R_N < \frac{n!}{\alpha_1^{p+1}} \left(\frac{\alpha_2}{\alpha_1}\right)^{N+1} \frac{(p+N+1)!}{(n+N+2)!}. \tag{54}$$

Passing to the integrals Ω_{np}, the optimal algorithm depends on the sign of n. Similarly as before, by inserting the integral representation of E_{-p}, Eq. (61), into Eq. (46) and exchanging the order of integrations

$$\Omega_{np}(\alpha_1, \alpha_2) = \int_1^\infty dz\, z^p\, e^{-\alpha_1 z} \int_1^\infty dt\, t^n\, e^{-\alpha_2 t z} = \int_1^\infty dz\, z^p\, e^{-\alpha_1 z}\, E_{-n}(\alpha_2 z). \tag{55}$$

When the values of n are positive one can use the recursive relation (63) which gives

$$\Omega_{np}(\alpha_1, \alpha_2) = \frac{n}{\alpha_2}\, \Omega_{n-1,p-1}(\alpha_1, \alpha_2) + \frac{1}{\alpha_2} E_{-p+1}(\alpha_1 + \alpha_2). \tag{56}$$

This recursion relation is completely stable when carried out in the upward direction along the "diagonal" lines. However, it is not self-starting and requires values of Ω_{n0} and Ω_{0p} to initiate. Analytical expression for the latter is fairly obvious, $\Omega_{0p} = E_{-p+1}(\alpha_1 + \alpha_2)$, and calculation of the former is based on the following relation

$$\Omega_{n0}(\alpha_1, \alpha_2) = \frac{e^{-\alpha_1}}{\alpha_2} E_{-n+1}(\alpha_2) - \frac{\alpha_1}{\alpha_2} \Omega_{n-1,0}(\alpha_1, \alpha_2), \tag{57}$$

starting with $\Omega_{00} = E_1(\alpha_1 + \alpha_2)$. This recursion is stable provided that the value of α_2 is moderate or large. If α_2 is small the following series expansion is used

$$\Omega_{n0}(\alpha_1, \alpha_2) = \frac{n!}{\alpha_2^{n+1}} E_{n+1}(\alpha_1) - \sum_{k=0}^{\infty} \frac{(-\alpha_2)^k}{k!} \frac{E_{-k}(\alpha_1)}{n+k+1}, \tag{58}$$

which can be derived by using elementary methods. Similarly as before one can verify that the absolute value of each term in the above sum is bounded by $\alpha_2^k/\alpha_1^{k+1}$ which can be used to estimate the convergence rate.

Finally, let us discuss calculation of Ω_{np} for negative values of n. The following recursion can be derived with help of Eqs. (46) and (63)

$$\Omega_{np}(\alpha_1, \alpha_2) = \frac{p}{\alpha_2} \Omega_{n-1,p-1}(\alpha_1, \alpha_2) - \frac{\alpha_1}{\alpha_2} \Omega_{n-1,p}(\alpha_1, \alpha_2) + \frac{e^{-\alpha_1}}{\alpha_2} E_{1-n}(\alpha_2), \tag{59}$$

which can be used to increase p at cost of n. This recursive relation introduces some instabilities into the calculation, but this fact is not significant as the values of p rarely exceed 10. To initiate the above recursion one requires the values of Ω_{n0}. Similarly as before, the following expression is straightforward to derive

$$\Omega_{n0}(\alpha_1, \alpha_2) = \frac{e^{-\alpha_1}}{\alpha_2} E_{1-n}(\alpha_2) - \frac{\alpha_1}{\alpha_2} \Omega_{n-1,0}(\alpha_1, \alpha_2). \tag{60}$$

Table 2 The functions $W_\mu(p;\alpha_1,\alpha_2)$ calculated for some representative values of the parameters

μ	Exact	Large-order expansion	Convergence
$\alpha_1 = 1.0, \alpha_2 = 1.0, p = 0$			
30	7.26 438 420 525 738 [−05]	7.26 438 420 525 741 [−05]	13
40	4.12 230 721 703 987 [−05]	4.12 230 721 703 989 [−05]	11
50	2.65 207 347 050 162 [−05]	2.65 207 347 050 163 [−05]	9
60	1.84 808 542 738 505 [−05]	1.84 808 542 738 506 [−05]	7
$\alpha_1 = 1.0, \alpha_2 = 5.0, p = 0$			
30	4.43 294 559 944 128 [−07]	4.43 294 559 944 129 [−07]	19
40	2.51 607 499 568 558 [−07]	2.51 607 499 568 559 [−07]	16
50	1.61 886 531 395 923 [−07]	1.61 886 531 395 924 [−07]	12
60	1.12 815 856 115 223 [−07]	1.12 815 856 115 224 [−07]	9
$\alpha_1 = 1.0, \alpha_2 = 10.0, p = 0$			
30	1.62 914 653 440 044 [−10]	1.62 914 653 440 043 [−10]	29
40	9.24 696 775 490 950 [−10]	9.24 696 775 490 946 [−10]	21
50	5.94 963 334 102 345 [−10]	5.94 963 334 102 343 [−10]	19
60	4.14 621 345 113 117 [−10]	4.14 621 345 113 115 [−10]	19
$\alpha_1 = 1.0, \alpha_2 = 50.0, p = 0$			
30	1.49 278 026 722 289 [−27]	Divergence	–
40	8.47 302 548 103 673 [−28]	Divergence	–
50	5.45 168 822 712 533 [−28]	Divergence	–
60	3.79 921 108 103 191 [−28]	3.79 921 108 103 191 [−28]	157
$\alpha_1 = 5.0, \alpha_2 = 5.0, p = 0$			
30	4.85 315 094 815 931 [−09]	4.85 315 094 815 933 [−09]	21
40	2.75 906 112 497 927 [−09]	2.75 906 112 497 928 [−09]	17
50	1.77 656 445 608 724 [−09]	1.77 656 445 608 724 [−09]	15
60	1.23 857 631 621 439 [−09]	1.23 857 631 621 440 [−09]	13
$\alpha_1 = 5.0, \alpha_2 = 10.0, p = 0$			
30	2.17 631 353 217 224 [−11]	2.17 631 353 217 225 [−11]	29
40	1.23 815 626 851 864 [−11]	1.23 815 626 851 865 [−11]	21
50	7.97 525 834 542 020 [−12]	7.97 525 834 542 023 [−12]	19
60	5.56 120 404 111 395 [−12]	5.56 120 404 111 398 [−12]	19
$\alpha_1 = 5.0, \alpha_2 = 50.0, p = 0$			
30	2.51 589 622 982 829 [−29]	Divergence	–
40	1.43 273 896 436 017 [−29]	Divergence	–
50	9.23 286 988 543 448 [−30]	Divergence	–
60	6.43 979 747 051 030 [−30]	6.43 979 747 051 030 [−30]	189
$\alpha_1 = 10.0, \alpha_2 = 10.0, p = 0$			
30	1.09 589 723 489 100 [−13]	1.09 589 723 489 100 [−13]	29
40	6.24 425 513 575 906 [−14]	6.24 425 513 575 909 [−14]	21
50	4.02 496 564 881 221 [−14]	4.02 496 564 881 222 [−17]	19
60	2.80 774 946 310 143 [−14]	2.80 774 946 310 144 [−17]	19

Table 2 continued

μ	Exact	Large-order expansion	Convergence
$\alpha_1 = 10.0, \alpha_2 = 50.0, p = 0$			
30	1.54 163 263 060 580 [−31]	Divergence	–
40	8.80 879 102 228 926 [−32]	Divergence	–
50	5.68 572 697 434 438 [−32]	Divergence	–
60	3.96 925 492 004 272 [−32]	Divergence	–

Exact denotes values calculated using explicit expressions (c.f. Ref. [29]) in extended arithmetic precision with the MATHEMATICA package (all digits shown are correct). *Large-order expansion* column shows results of calculations with Eq. (33) in the double precision arithmetic. *Convergence* denotes a number of terms in Eq. (33) required to converge the summation to relative precision of 2×10^{-16}. The symbol [k] denotes the powers of 10, 10^k

Table 3 The functions $W_\mu(p; \alpha_1, \alpha_2)$ calculated for some representative values of the parameters

μ	Exact	Large-order expansion	Convergence
$\alpha_1 = 1.0, \alpha_2 = 1.0, p = 8$			
30	8.57 988 797 367 550 [−02]	8.57 988 797 367 554 [−02]	13
40	4.83 735 222 300 728 [−02]	4.83 735 222 300 730 [−02]	11
50	3.10 265 767 847 292 [−02]	3.10 265 767 847 291 [−02]	9
60	2.15 848 287 860 469 [−02]	2.15 848 287 860 470 [−02]	9
$\alpha_1 = 1.0, \alpha_2 = 5.0, p = 8$			
30	3.76 412 026 039 309 [−06]	3.76 412 026 039 311 [−06]	19
40	2.10 468 765 565 305 [−06]	2.10 468 765 565 306 [−06]	17
50	1.34 482 396 704 125 [−06]	1.34 482 396 704 126 [−06]	15
60	9.33 659 812 480 290 [−07]	9.33 659 812 480 295 [−07]	13
$\alpha_1 = 1.0, \alpha_2 = 10.0, p = 8$			
30	4.37 682 376 980 937 [−09]	4.37 682 376 980 939 [−09]	29
40	2.45 407 770 819 367 [−09]	2.45 407 770 819 369 [−09]	21
50	1.57 011 062 044 134 [−09]	1.57 011 062 044 135 [−09]	19
60	1.09 084 224 914 003 [−09]	1.09 084 224 914 004 [−09]	19
$\alpha_1 = 1.0, \alpha_2 = 50.0, p = 8$			
30	1.79 779 640 123 314 [−27]	Divergence	–
40	1.01 180 529 453 933 [−27]	Divergence	–
50	6.48 466 217 722 202 [−28]	Divergence	–
60	4.50 946 436 202 621 [−28]	4.50 946 436 202 621 [−28]	181
$\alpha_1 = 5.0, \alpha_2 = 5.0, p = 8$			
30	1.44 602 672 357 563 [−08]	1.44 602 672 357 562 [−08]	21
40	8.19 252 305 004 658 [−09]	8.19 252 305 004 661 [−09]	17
50	5.26 663 146 433 895 [−09]	5.26 663 146 433 898 [−09]	15
60	3.66 849 871 467 375 [−09]	3.66 849 871 467 377 [−09]	13

Table 3 continued

μ	Exact	Large-order expansion	Convergence
$\alpha_1 = 5.0, \alpha_2 = 10.0, p = 8$			
30	4.24 176 585 818 655 [−11]	4.24 176 585 818 656 [−11]	29
40	2.40 082 417 196 577 [−11]	2.40 082 417 196 578 [−11]	21
50	1.54 267 805 985 739 [−11]	1.54 267 805 985 739 [−11]	19
60	1.07 428 909 373 431 [−11]	1.07 428 909 373 431 [−11]	19
$\alpha_1 = 5.0, \alpha_2 = 50.0, p = 8$			
30	2.98 140 021 972 450 [−29]	Divergence	–
40	1.68 614 952 443 023 [−29]	Divergence	–
50	1.08 306 875 847 441 [−29]	Divergence	–
60	7.54 082 251 283 390 [−30]	Divergence	–
$\alpha_1 = 10.0, \alpha_2 = 10.0, p = 8$			
30	1.75 800 825 092 494 [−13]	1.75 800 825 092 495 [−13]	29
40	9.99 225 776 925 089 [−14]	9.99 225 776 925 094 [−14]	21
50	6.43 335 525 002 640 [−14]	6.43 335 525 002 643 [−14]	19
60	4.48 491 212 960 371 [−14]	4.48 491 212 960 374 [−14]	19
$\alpha_1 = 10.0, \alpha_2 = 50.0, p = 8$			
30	1.79 687 571 912 046 [−31]	Divergence	–
40	1.02 110 421 809 320 [−31]	Divergence	–
50	6.57 355 034 007 000 [−32]	Divergence	–
60	4.58 239 720 894 004 [−32]	Divergence	–

Exact denotes values calculated using explicit expressions (c.f. Ref. [29]) in extended arithmetic precision with the MATHEMATICA package (all digits shown are correct). *Large-order expansion* column shows results of calculations with Eq. (33) in the double precision arithmetic. *Convergence* denotes a number of terms in Eq. (33) required to converge the summation to relative precision of 2×10^{-16}. The symbol [k] denotes the powers of 10, 10^k

This recursion relation is carried out downward, starting with $\Omega_{-N,0}$ at some large N. This completes the formalism of calculation of the basic integrals.

4.5 Numerical tests and examples

In Tables 2 and 3 we present results of exemplary calculations of the $W_\mu(p; \alpha_1, \alpha_2)$ functions with Eq. (47) and comparison with the exact results. One can see that the method based on Eq. (47) converges in at most few tens of terms provided that α_1 and α_2 are both small or moderate. In fact, for small values of the nonlinear parameters we managed to obtain the convergence even for μ as small as 10 which shows the potential of the method. Unfortunately, when α_1 and α_2 are both large (larger than 50, say) the series (47) have an oscillatory behaviour and no convergence was achieved after summing 200 terms. However, in the regime of large α_1 and α_2 one can resort to different techniques e.g. asymptotic expansions presented in Ref. [29]. Moreover, when α_1 and α_2 are simultaneously large the resulting integrals are expected to be very

small and they are likely to be negligible. Table 2 lists the results for $p = 0$ whilst the corresponding values for $p = 8$ are given in Table 3. A more detailed comparison reveals that larger values of p are connected with slower convergence of the series (47), but the range of applicability remains roughly the same.

5 Conclusions

We have presented a new systematic approach to the calculation of basic quantities appearing in the ellipsoidal expansion of the two-electron integrals over Slater-type orbitals. Large-order (μ) expansions of the functions L_μ and W_μ have been given and their accuracy and range of applicability has been determined numerically. The new method allows to calculate higher-order terms of the Neumann expansion with a significantly reduced computational cost. As a result, this is a step towards reduction of the gap in computational timings between STOs and GTOs. Moreover, the presented expressions may be useful in mathematical studies of convergence of the Neumann series and rational design of convergence acceleration techniques.

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Appendix 1: Auxiliary integrals

Virtually all final working formulae obtained in the present paper are given in terms of the basic integrals $E_n(z)$ and $a_n(z)$. They are defined through the integral representations

$$E_n(z) = \int_1^\infty dt\, \frac{e^{-zt}}{t^n}, \tag{61}$$

$$a_n(z) = \int_0^1 dt\, t^n e^{-zt}, \tag{62}$$

where n is an arbitrary integer in the former and a nonnegative integer in the latter. Calculation of a_n is most easily carried out with help of the Miller algorithm [49] as discussed by Harris [22]. The integral E_n is usually called the generalised exponential integral. Computation of E_n differs depending on the sign of n. For a negative integer n the following recursion is completely stable in the upward direction

$$E_n(z) = -\frac{n}{z} E_{n-1}(z) + \frac{e^{-z}}{z}. \tag{63}$$

For positive n and $z < 1$ one uses the series expansion

$$E_n(z) = \frac{(-z)^{n-1}}{(n-1)!} \left[\Psi(n) - \log z\right] - \sum_{\substack{k=0 \\ k \neq n-1}}^{\infty} \frac{(-z)^k}{k!\,(1-n+k)}, \tag{64}$$

where $\Psi(n)$ is the digamma function at integer argument. The above infinite summations converge to the machine precision in, at most, few tens of terms. Finally, for positive n and $z > 1$ the continued fraction (CF) formula can be applied

$$E_n(z) = e^{-z}\left(\frac{1}{z+}\frac{p}{1+}\frac{1}{z+}\frac{p+1}{1+}\frac{2}{z+}\cdots\right). \tag{65}$$

To evaluate the CF one can use the Lentz algorithm [43]. The only inconvenience is that consecutive numerators and denominators in the Lentz scheme grow very quickly with the number of terms retained in Eq. (65). Therefore, it is necessary to rescale them from time to time by a small number to avoid numerical overflows. Let us also recall the leading terms of the large-order asymptotic expansions for $E_n(z)$ and $a_n(z)$ which read

$$E_n(z) = \frac{e^{-z}}{n+z} + \mathcal{O}\left(\frac{1}{n^2}\right), \tag{66}$$

$$a_n(z) = \frac{e^{-z}}{n-z} + \mathcal{O}\left(\frac{1}{n^2}\right), \tag{67}$$

where $n > z$.

Appendix 2: Large-order asymptotic formulae for $i_\mu(\alpha)$ and $k_\mu(\alpha)$

According to the work of Sidi et al. [47,48] the modified spherical Bessel functions posses the following large-order expansions

$$i_\mu(z) = \frac{\sqrt{\pi}}{2}\frac{(z/2)^\mu}{\Gamma(\mu+\frac{3}{2})}\sum_{m=0}^{\infty}\frac{b_m(z)}{(\mu+1/2)^m}, \tag{68}$$

$$k_\mu(z) = \frac{\sqrt{\pi}}{4}\frac{\Gamma(\mu+\frac{1}{2})}{(z/2)^{\mu+1}}\sum_{m=0}^{\infty}\frac{b_m(z)}{(\mu+1/2)^m}(-1)^m, \tag{69}$$

as $\mu \to \infty$ at a fixed z, where

$$b_m(z) = \sum_{k=1}^{m}(-1)^{m-k}\frac{S_{mk}}{k!}(z/2)^{2k}, \tag{70}$$

for $m > 0$ and $b_0(z) = 1$. The quantities S_{mk} in the above expression are the Stirling numbers of the second kind [43] defined recursively as

$$S_{m0} = \delta_{m0}, \quad S_{m1} = 1, \quad S_{mm} = 1, \tag{71}$$

$$S_{mk} = S_{m-1,k-1} + kS_{m-1,k}, \tag{72}$$

and we additionally adapt the convention $S_{mk} = 0$ for $m < k$ or $m < 0$.

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Paper V

"Combining Slater-type orbitals and effective core potentials"

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Commentary

In this paper we make the first step towards an application of the Slater-type orbitals in accurate calculations for heavy diatomic molecules where the relativistic effects become important. We adopt one of the most popular methods for handling such systems based on the so-called effective core potentials (ECPs). These pseudopotentials replace a fraction of core electrons of an atom by an effective potential designed to reproduce fully relativistic theoretical results (Dirac-Hartree-Fock etc.) or some reference experimental data such as the atomic spectra. Additional benefits of ECPs are that the core electrons are not treated explicitly (which reduces the computational costs) and the spin-orbit coupling effects can easily be included in a similar manner.

The main difficulties in combining ECPs with STOs originate from the functional form of the pseudopotentials. Despite formally written as one-electron operators, ECPs contain projection operators on the angular momenta at the atomic site. In other words, ECPs are non-local operators and the result of their action depends on the angular momentum of a function they operate on. Moreover, the radial components of the pseudopotentials are usually represented as linear combinations of the Gaussian functions. This leads to various mixed Gaussian-Slater integrals which are

resistant to the standard techniques based on, e.g. the ellipsoidal coordinates.

To solve these problems we adopt an approach based on the Barnett-Coulson translation method. When all quantities present in the integrand are shifted to the common centre the action of the projection operators can be resolved relatively easily. This reduces the problem to calculation of various radial (i.e. one-dimensional) integrals for which a family of recursive techniques is proposed. As mentioned in the previous sections, the most troublesome aspect of the Barnett-Coulson method is the fact it involves infinite summations. Fortunately, in the case of ECPs matrix elements all such summations truncate after a finite number of terms facilitating an efficient and stable implementation. In the same spirit we solve matrix elements of the related core polarisation potentials and effective spin-orbit potentials.

The reliability of the proposed approach is illustrated by a number of numerical examples. First, we develop accurate STOs basis sets for the alkaline earth metals (Ca, Sr, Ba). Very good results are obtained for the atomic spectra, static dipole polarisabilities, and valence orbital energies of these atoms. Next, we move to the calculations for the molecular systems. We evaluate interaction energies, permanent dipole moments, and ionisation energies for the barium and strontium hydrides (BaH and SrH). Comparison with the available experimental data confirms the validity of the proposed method.

Combining Slater-type orbitals and effective core potentials

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We present a general methodology to evaluate matrix elements of the effective core potentials (ECPs) within a one-electron basis set of Slater-type orbitals (STOs). The scheme is based on translation of individual STO distributions in the framework of the Barnett-Coulson method. We discuss different types of integrals which naturally appear and reduce them to a few basic quantities which can be calculated recursively or purely numerically. Additionally, we consider evaluation of the STOs matrix elements involving the core polarization potentials and effective spin-orbit potentials. Construction of the STOs basis sets designed specifically for use with ECPs is discussed and differences in comparison with all-electron basis sets are briefly summarized. We verify the validity of the present approach by calculating excitation energies, static dipole polarizabilities, and valence orbital energies for the alkaline-earth metals (Ca, Sr, and Ba). Finally, we evaluate interaction energies, permanent dipole moments, and ionization energies for barium and strontium hydrides, and compare them with the best available experimental and theoretical data.

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I. INTRODUCTION

In the past 40 years, Gaussian-type orbitals [1,2] (GTOs) have undeniably taken the role of the routine one-electron basis set for *ab initio* calculations in molecular physics and quantum chemistry. Nonetheless, a considerable interest has remained in the field of Slater-type orbitals (STOs) [3,4] or more general exponential-type orbitals (ETOs) [5,6]. This is motivated mainly by the superior analytical properties of STOs (i.e., fulfillment of the nuclear cusp condition [7] and correct long-range decay [8,9]) and their formal simplicity.

The biggest obstacle connected with use of STOs is calculation of many-center two-electron integrals which are unavoidable in any molecular study. Interestingly enough, there has been a significant progress on this issue in recent years. In fact, looking at only the past 15 years, there are many notable works of Bouferguene *et al.* [10–13], Rico *et al.* [14–24], Hoggan *et al.* [25–30], Pachucki [31–35], and others [36–52]. In particular, for the diatomic systems STOs can now be used routinely [51].

State-of-the-art *ab initio* electronic structure calculations are important for the new field at the border of chemistry and physics—studies of ultracold molecules. Experimental advances in laser cooling and trapping of neutral atoms have opened a door for the formation of ultracold diatomic molecules by photoassociation [53], magnetoassociation [54], and vibrational cooling [55] techniques. To interpret the experimental observations, *ab initio* calculations of the potential-energy curves and coupling matrix elements between the electronic states are crucial. Somewhat surprisingly, spectroscopic and collisional studies of ultracold molecules mostly involve molecules with heavy atoms. See, for instance, Refs. [56–61] for joint experimental and theoretical studies of new spectroscopic features of the strontium molecule. Electronic structure calculations can also be used to predict new schemes for the formation of ultracold diatomic molecules [62–67]. Accurate interatomic interaction potentials are also of great importance in the search for a new physics; see, e.g., the work on the YbF molecule which is used in measurements of the permanent electric dipole moment (EDM) of the electron [68], and determination of the proton-electron mass ratio time variation [69]. One can also point out the work of Schwerdtfeger *et al.* [70] on the Sr_2 molecule where time dependence of the fine-structure constant is considered. Other examples of physically important diatoms include RbYb molecule [71–73] (a promising candidate for quantum computing), BaH [74–76] (preparation of ultracold hydrogen atoms), and others.

It must be stressed that in a majority of the studies mentioned above, accurate first principles calculations were fundamental in understanding and interpretation of the experimental data. In particular, computations of the potential-energy surfaces and the corresponding coupling matrix elements appear to be of prime importance. This is also the area where the Slater-type orbitals are the most advantageous.

Unfortunately, in accurate *ab initio* calculations for heavy elements one typically encounters two additional major problems. First, the number of occupied orbitals becomes fairly substantial. This, by necessity, calls for extended basis sets with high angular momenta, increasing the overall cost of correlated electronic structure calculations. The second obstacle is the relative importance of the relativistic effects; for heavier elements they are of a similar magnitude (or larger) as the electron correlation contribution [77,78]. Moreover, additivity of the latter two effects for heavy atoms is at best questionable [77,78].

There are several approaches available in the literature to handle the aforementioned problems and most of them are based on the Dirac-Coulomb(-Breit) equations [79,80]. This is done, e.g., by constructing an approximate four-component spinor expanded in a kinetically balanced basis set [81–84], or by decoupling the small and large components of the spinor, so that the equations take a familiar two-component form [85–92]. Another idea developed independently relies on the so-called regular approximations [93,94]. In this paper we consider the effective core potential (ECP) approach [95] which may be viewed as a slightly less rigorous method than the former ones. However, little accuracy is typically sacrificed

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(especially for weakly bound systems) and the calculations simplify to a great extent.

The fundamental idea behind ECPs is that the inner core orbitals of heavy elements are inert and do not change significantly in different chemical environments. Therefore, their influence on the valence space can be modeled with a proper pseudopotential (PP) [96] which is, by definition, universal for a given element. This leads to an approximate two-component valence relativistic wave function, obtained as an eigenfunction of the *valence only* Hamiltonian. This approach has two unquestionable advantages. First, the inner core orbitals are removed from explicit consideration, so that the size of the one-electron basis set is considerably reduced. Second, the scalar relativistic effects can be straightforwardly included in the pseudopotential (by a proper parametrization).

The main goal of this work is to combine the methodology of effective core potentials with the one-electron basis set of Slater-type orbitals. We propose a general method to evaluate all necessary matrix elements by using analytical or seminumerical techniques. Efficiency of the proposed algorithm is sufficient to perform general large-scale calculations. Further in the paper, we consider the so-called core polarization potentials [97–99] which rely on the assumption that the core is additionally polarizable. This captures the first-order effects of the implicit core-valence correlations and significantly improves the description when the large-core pseudopotentials are used. We also briefly consider effective spin-orbit pseudopotentials [100–102] which allow for an approximate computation of the spin-orbit splittings and couplings. Finally, we present results of test calculations for alkaline-earth metals (Ca, Sr, and Ba) and predict properties of the corresponding hydrides.

In the paper we rely on the known special functions to simplify the derivations and the final formulas. Our convention for all special functions appearing below is the same as in Ref. [103].

II. THEORY

In this section we introduce some important formulas which are used further in the paper. This is necessary to introduce the notation and specify precise meaning of several quantities. This short mathematical preface may be useful for readers who are not entirely familiar with employed concepts.

A. Slater-type orbitals and spatial translations

Slater-type orbitals (STOs) [3,4] have the following general form:

$$\chi_{nlm}(\mathbf{r};\beta) = r^{n-1}e^{-\beta r}\,Y_{lm}(\theta,\phi), \tag{1}$$

where Y_{lm} are the spherical harmonics defined according to the Condon-Shortley phase, n, l are nonnegative integers satisfying $n > l$, and $\beta > 0$ is a real parameter. The orbitals defined above are not normalized; we find this convention to be more robust for the purposes of the paper. In order to restore the proper unity normalization Eq. (1) has to be multiplied by $S_n(\beta) = (2\beta)^{n+1/2}/\sqrt{(2n)!}$.

Throughout the paper we shall extensively use the translation method for STOs in order to shift them to a convenient point in space. This is achieved with help of the famous Barnett-Coulson ζ-function method [104–106]. Translation of the *ns* STOs is given by the following two-range formula:

$$r_b^{n-1}e^{-\beta r_b} = \sum_{m=0}^{\infty}\frac{2k+1}{2}\,P_m(\cos\theta_a)\,\zeta_{nm}(\beta,r_a;R), \tag{2}$$

where P_m are the ordinary Legendre polynomials, R is the distance between centers a and b, and ζ_{nm} are given by the integral representation

$$\zeta_{nm}(\beta,r_a;R) = \int_0^{\pi} d\theta_a\,\sin\theta_a\,P_m(\cos\theta_a)\,r_b^{n-1}\,e^{-\beta r_b}. \tag{3}$$

From now on, we drop the parentheses from the definition of the ζ function, i.e., it is assumed that $\zeta_{nm} := \zeta_{nm}(\beta,r_a;R)$ unless explicitly stated otherwise.

The above formal definitions are not particularly useful in actual applications. Instead, the following recursive relations provide a starting point for further developments:

$$\zeta_{n+2,m} = \left(r_a^2+R^2\right)\zeta_{nm} - \frac{2\,r_a\,R}{2m+1} \times\left[m\,\zeta_{n,m-1} + (m+1)\,\zeta_{n,m+1}\right] \tag{4}$$

and

$$\zeta_{1m} = \frac{\beta\,r_a\,R}{2m+1}[\zeta_{0,m-1} - \zeta_{0,m+1}]. \tag{5}$$

The last formula is not valid for $m = 0$ and the explicit expression should be used instead,

$$\zeta_{10} = \beta\,r_a\,R[\zeta_{00} - \zeta_{01}] + e^{-\beta(r_a+R)}. \tag{6}$$

To initiate the recursive process one requires the following starting values:

$$\zeta_{0m} = \frac{2\beta}{\pi}\,i_m(\beta\,r_<)\,k_m(\beta\,r_>), \tag{7}$$

where i_m and k_m are the modified spherical Bessel functions of the first and second kind [103], respectively, and $r_< = \min(r_a,R)$, $r_> = \max(r_a,R)$. For convenience of the reader, we gathered all properties of the modified spherical Bessel functions which are important here in the Supplemental Material [107]. Equations in the Supplemental Material are referenced with prefix "S", e.g., the sixth equation in the Supplemental Material is referenced as Eq. (S6).

In order to spatially shift STOs of the form (1) one needs to combine Eq. (2) with the well-known translation formula for the regular solid harmonics, Ref. [108], pp. 797. This leads to

$$\begin{aligned}\frac{1}{\sqrt{\pi}}\,r_b^{n-1}\,e^{-\beta r_b}\,Y_{lm}(\theta_b,\phi_b) &= (-1)^{l-m}\,(2l+1)\sum_{\lambda=0}^{l}\frac{r_a^{\lambda}}{\sqrt{2\lambda+1}}\,Y_{\lambda m}(\theta_a,\phi_a)\,(-R)^{l-\lambda} \\ &\times\begin{pmatrix}\lambda & l-\lambda & \lambda\\ m & 0 & -m\end{pmatrix}\begin{pmatrix}2l\\ 2\lambda\end{pmatrix}^{1/2} \\ &\times\sum_{k=0}^{\infty}\sqrt{2k+1}\,Y_{k0}(\theta_a,\phi_a)\,\zeta_{n-l,k}(\beta,r_a;R),\end{aligned} \tag{8}$$

with the usual notation for the Wigner $3J$ symbols, Ref. [108], pp. 270.

A short comment on the nature of the above expression is necessary. It is well known that the strongest drawback of the Barnett-Coulson method is that it leads, in general, to infinite series. Worse than that, these series tend to converge extremely slowly; in some cases a logarithmic convergence pattern has been observed [109,110]. This limits the applicability of the method significantly and forced some authors to apply convergence acceleration techniques [111,112]. Fortunately, this issue is absent in *all* final formulas derived in this paper. In most cases, the sum over k truncates as a result of the triangle conditions for the Wigner $3J$ symbols; see Ref. [108], pp. 803.

Before the end of the present section we would like to point out that there exist some other methods for translation of STOs, including one-range and two-range formulas, Refs. [113–123], yet we have not found these alternative formulations to be particularly advantageous in the present case compared to the standard Barnett-Coulson scheme, Eq. (8). General theory of addition theorems was given in a pedagogical way by Weniger [38,39]. Note that mathematical correctness (and usefulness) of some formulations of the addition theorems is still subject to a debate [40].

B. Pseudopotentials parametrization

As already mentioned in the Introduction, in calculations involving ECPs one considers the following valence-only Hamiltonian [95]:

$$\hat{H}_v = \sum_i^{n_v}\left[-\frac{1}{2}\nabla_i^2 + \sum_a\left[-\frac{Q_a}{r_{ia}} + \hat{U}^a_{\rm PP}(r_{ia})\right]\right] + \sum_{i<j}^{n_v}\frac{1}{r_{ij}} + \sum_{ab}\frac{Q_aQ_b}{r_{ab}} + \hat{U}_{\rm CPP}, \tag{9}$$

where $i,j,\ldots$ denote the electrons, $a,b,\ldots$ denote the nuclei, $\hat{U}^a_{\rm PP}$ is the pseudopotential of the core a with charge Q_a, and n_v is the number of valence electrons. The term arising from the core polarization potential ($\hat{U}_{\rm CPP}$) will be specified further in the text.

Let us briefly discuss the construction of the effective core potentials. They are divided into the spin-averaged and spin-dependent terms, $U^a_{\rm PP} = U^a_{\rm PP,av} + U^a_{\rm PP,so}$. Typically, the first term is included explicitly in the electronic structure calculations while the second is treated perturbatively. Both of these potentials are represented in a semilocal form

$$\hat{U}^a_{\rm PP,av}(r_{ia}) = U^a_L(r_{ia}) + \sum_{l=0}^{L-1}\sum_{m=-l}^{+l}|lm\rangle_a \times \left[U^a_l(r_{ia}) - U^a_L(r_{ia})\right]_a\langle lm| \tag{10}$$

and

$$\hat{U}^a_{\rm PP,so}(r_{ia}) = \sum_{l=0}^{L-1}\sum_{m=-l}^{+l}\frac{2\,\Delta U^a_l(r_{ia})}{2l+1}\,|lm\rangle_a\,\mathbf{l}_{ia}\cdot\mathbf{s}_i\,{}_a\langle lm|, \tag{11}$$

where L is the highest angular momentum of the orbitals in the core a, $\mathbf{l}_{ia}$ is the (orbital) angular momentum operator corresponding to the center a and the electron i, $\mathbf{s}_i$ is the spin operator of the electron i, and $\langle lm|_a$ are projection operators on the spherical harmonics Y_{lm} placed at the center a. Presence of the projection operators assures that orbital components of different angular momenta connect with proper radial functions. Parenthetically, it is observed that $U^a_l(r_{ia})$ are nearly identical for $l > L$ which justifies the rearrangements in Eqs. (10) and (11).

To specify a family of pseudopotentials a precise form of the radial components, $U^a_l(r)$, must be given. It is very common to use a short linear combination of the radial Gaussian functions [95]

$$r^2\,U^a_l(r) = \sum_k A^a_{kl}\,r^{n_{kl}}e^{-B^a_{kl}r^2}, \tag{12}$$

where n_{kl}, A^a_{kl}, and B^a_{kl} are adjustable parameters. Their determination for a given atom is far from trivial and strategies of the so-called energy-consistent [124–127], shape-consistent [128–131], and other [95] pseudopotentials were developed.

C. Effects of the core polarization

The so-called core polarization potentials [97–99] (CPP) constitute a method to improve upon the approximations underlying the ordinary ECPs. The core is allowed to be polarizable, i.e., reorientation of valence electrons in a molecular environment creates an induced dipole moment of the core. By simple electrostatic arguments, the value of this dipole moment is assumed to be proportional to the strength of the electric field at the core. This gives rise to the total potential $\hat{U}_{\rm CPP} = \sum_a \hat{U}^a_{\rm CPP}$ in the form

$$\hat{U}^a_{\rm CPP} = \hat{U}^{[0],a}_{\rm CPP} + \hat{U}^{[1],a}_{\rm CPP} + \hat{U}^{[2],a}_{\rm CPP}, \tag{13}$$

$$\hat{U}^{[0],a}_{\rm cpp} = -\frac{1}{2}\alpha_a\sum_{b,c\neq a}Q_bQ_c\frac{\mathbf{R}_{ab}\cdot\mathbf{R}_{ac}}{R^3_{ab}R^3_{ac}}, \tag{14}$$

$$\hat{U}^{[1],a}_{\rm cpp} = -\frac{1}{2}\alpha_a\sum_i\frac{1}{r^4_{ia}}C^2(r_{ia},\delta_a) + \alpha_a\sum_i\sum_{b\neq a}Q_b\frac{\mathbf{r}_{ia}\cdot\mathbf{R}_{ab}}{r^3_{ia}R^3_{ab}}C(r_{ia},\delta_a), \tag{15}$$

$$\hat{U}^{[2],a}_{\rm cpp} = -\alpha_a\sum_{j<i}\frac{\mathbf{r}_{ia}\cdot\mathbf{r}_{ja}}{r^3_{ia}r^3_{ja}}C(r_{ia},\delta_a)\,C(r_{ja},\delta_a), \tag{16}$$

where the consecutive terms are the scalar, one-, and two-electron components. In the above expression α_a is the polarizability of the core a, determined from separate theoretical calculations or by semiempirical adjustment; $C(r_{ia},\delta_a)$ is the cutoff function assuring that the potential is regular when electron i is at the core a. The form of the cutoff function as well as the value of the cutoff parameter δ_a are arbitrary. The following expression is frequently used:

$$C(r,\delta) = (1-e^{-\delta r^2})^{\bar{n}}, \tag{17}$$

where $\bar{n}$ is either 1 (Stoll and Fuentealba [97]) or 2 (Müller and Meyer [98,99]). The optimal values of δ_a are determined by numerical experimentation for each atom separately.

D. Basic integrals

Further in the text we show that all matrix elements involving averaged and spin-orbit pseudopotentials can be expressed through the following family of one-dimensional integrals:

$$\mathcal{F}_n^0(x,y) = \int_0^\infty dr\, r^n\, e^{-xr-yr^2}, \tag{18}$$

$$\mathcal{F}_n^>(x,y) = \int_1^\infty dr\, r^n\, e^{-xr-yr^2}, \tag{19}$$

$$\mathcal{F}_n^<(x,y) = \int_0^1 dr\, r^n\, e^{-xr-yr^2}. \tag{20}$$

For evaluation of the core polarization potentials matrix elements one additionally requires integrals with a logarithmic (albeit integrable) singularity, e.g.,

$$\mathcal{G}_n^0(x,y) = \int_0^\infty dr\ \ln r\, r^n\, e^{-xr-yr^2}, \tag{21}$$

and similarly for $\mathcal{G}_n^>$ and $\mathcal{G}_n^<$.

The issue of calculation of the above integrals is fairly technical and marred with numerical problems. For completeness, in the Supplemental Material [107] we present an exhaustive description of the methods we recommend for calculation of these basic quantities. Additionally, a special case of these integrals was considered in Ref. [132]. Note that Eqs. (18) and (20) are well defined only for $n \geqslant 0$; this restriction does not hold for Eq. (19).

III. SPIN-AVERAGED AND SPIN-ORBIT MATRIX ELEMENTS

In the remainder of the paper we consider calculation of ECPs matrix elements for diatomic systems only. This is mainly because the issue of exact calculation of the two-electron integrals for polyatomic molecules has not been fully resolved yet. Consequently, we adopt a coordinate system where both atoms are located on the z axis and separated by a distance R.

For calculations on general polyatomic systems one needs the following matrix elements involving the spin-averaged potentials:

$$I_{\mathrm{bca}} = \left\langle \chi_{n_b l_b m_b}(\mathbf{r}_b;\beta_b)\right| \hat{U}^c_{\mathrm{PP,av}}(r_c)\left|\chi_{n_a l_a m_a}(\mathbf{r}_a;\beta_a)\right\rangle. \tag{22}$$

By using Eq. (10) and after simple manipulations one can rewrite the above expression as

$$I_{\mathrm{bca}} = I^{\mathrm{loc}}_{\mathrm{bca}} + I^{\mathrm{nloc}}_{\mathrm{bca}}, \tag{23}$$

where

$$I^{\mathrm{loc}}_{\mathrm{bca}} = \left\langle \chi_{n_b l_b m_b}(\mathbf{r}_b;\beta_b)\right| U^c_L(r_c)\left|\chi_{n_a l_a m_a}(\mathbf{r}_a;\beta_a)\right\rangle \tag{24}$$

and

$$I^{\mathrm{nloc}}_{\mathrm{bca}} = \sum_{KM}^{L-1}\int_0^\infty dr_c\, r_c^2\left\langle \chi_{n_b l_b m_b}(\mathbf{r}_b;\beta_b)|KM\right\rangle_c \times \left[U^c_K(r_c) - U^c_L(r_c)\right]_c\left\langle KM|\chi_{n_a l_a m_a}(\mathbf{r}_a;\beta_a)\right\rangle. \tag{25}$$

The approach adopted here depends on the relative location of the centers.

The main difficulty connected with the calculation of the pseudopotentials matrix elements is the presence of the projection operators if the orbitals are placed on different centers. Additionally, pseudopotentials are typically parametrized in terms of the Gaussian-type expansions, Eq. (12), which leads to mixed Slater-Gaussian type basic integrals. The latter are usually not easily expressible through the standard elementary and special functions, and new techniques need to be developed to handle them.

A. Spin-averaged potentials, I_{aaa} type

Let us first consider the atomic case, $a = b = c$. Due to orthogonality of the spherical harmonics the matrix element simplifies to

$$I_{\mathrm{aaa}} = I^{\mathrm{loc}}_{\mathrm{aaa}} + I^{\mathrm{nloc}}_{\mathrm{aaa}} = \begin{cases} \left\langle \chi_{n'_a l'_a m}(\mathbf{r}_a;\beta'_a)\right| U^a_L(r_a)\left|\chi_{n_a l_a m}(\mathbf{r}_a;\beta_a)\right\rangle, & l_a \geqslant L, \\ \left\langle \chi_{n'_a l'_a m}(\mathbf{r}_a;\beta'_a)\right| U^a_{l_a}(r_a)\left|\chi_{n_a l_a m}(\mathbf{r}_a;\beta_a)\right\rangle, & l_a < L, \end{cases} \tag{26}$$

provided that $l_a = l'_a$ and $m_a = m'_a = m$. Otherwise, the result vanishes due to the spherical symmetry of the integrand. Evaluation of the remaining integrals is now elementary; making use of Eqs. (1) and (12),

$$I_{\mathrm{aaa}} = \sum_k A^a_{kl}\, \mathcal{F}^0_{n_a+n'_a+n_{kl}-2}\left(\beta_a+\beta'_a, B^a_{kl}\right), \tag{27}$$

where $\mathcal{F}_n^0(x,y)$ is defined by Eq. (18).

B. Spin-averaged potentials, I_{baa} type

Let us now consider the first of the two-center matrix elements, I_{baa}. One can easily see that they obey formally the same expression as (26), but l_a and l_b do not need to be equal. However, the requirement $m_a = m_b$ still holds as a consequence of the axial symmetry. Translating STO from the center b to the point a

$$\frac{(-1)^{l_b}}{\sqrt{2l_a+1}}\langle \chi_{n_b l_b m}(\mathbf{r}_b;\beta_b)|\, U^a_L(r_a)\,|\chi_{n_a l_a m}(\mathbf{r}_a;\beta_a)\rangle = \frac{2l_b+1}{2}\sum_{\lambda=0}^{l_b}\begin{pmatrix}2l_b\\2\lambda\end{pmatrix}^{1/2}\begin{pmatrix}\lambda & l_b-\lambda & l_b\\ m & 0 & -m\end{pmatrix}(-R)^{l_b-\lambda}\mathcal{A}_\lambda, \tag{28}$$

where

$$\mathcal{A}_\lambda = \sum_k (2k+1)\begin{pmatrix}\lambda & k & l_a\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\lambda & k & l_a\\ m & 0 & -m\end{pmatrix} \times \sum_m A^a_{mL}\, W_{\lambda+n_a+n_{mL}-1,n_b-l_b,k}(\beta_a,\beta_b,B_{mL};R). \tag{29}$$

The remaining one-dimensional integration is confined to the following formula:

$$W_{lmn}(\alpha,\beta,\gamma;R) = \int_0^\infty dr\, r^l\, \zeta_{mn}(\beta,r;R)\, e^{-\alpha r-\gamma r^2}. \tag{30}$$

A straightforward approach to Eq. (30) is to use a quadrature of some sort and treat the integrals in a purely numerical fashion. However, the integrand possesses a derivative discontinuity (i.e., a cusp) at $r = R$. This makes integration with standard Gaussian quadratures difficult. For a reasonable performance one would need to divide the integration range into two subintervals, $[0,R]$ and $[R,\infty]$, and treat each of them separately, possibly with different integration rules. This, in turn, increases the computational costs as the integration needs to be performed for a large set of parameters l, m, n.

An alternative approach which we propose here relies on the recursive relations (4) and (5). By inserting them into the definition (30) one arrives at

$$W_{l,m+2,n} = W_{l+2,mn} + R^2\, W_{lmn} - \frac{2R}{2n+1} \times [n\, W_{l+1,m,n-1} + (n+1) W_{l+1,m,n+1}], \quad (31)$$

$$W_{l1n} = \frac{\beta R}{2n+1}[W_{l+1,0,n-1} - W_{l+1,0,n+1}], \quad (32)$$

and

$$W_{l10} = \beta R[W_{l+1,00} - W_{l+1,01}] + e^{-\beta R}\mathcal{F}_l^0(\alpha+\beta,\gamma). \quad (33)$$

To initiate the above recursions one needs W_{l0n}, which can be expressed with help of Eq. (7) as

$$W_{l0n} = \frac{2\beta}{\pi} R^{l+1}[k_n(\beta R)\,\mathcal{I}_{ln}(\alpha R,\beta R,\gamma R) + i_n(\beta R)\,\mathcal{K}_{ln}(\alpha R,\beta R,\gamma R)], \quad (34)$$

where

$$\mathcal{I}_{ln}(\alpha,\beta,\gamma) = \int_0^1 dx\, x^l\, i_n(\beta x)\, e^{-\alpha x-\gamma x^2}, \quad (35)$$

$$\mathcal{K}_{ln}(\alpha,\beta,\gamma) = \int_1^\infty dx\, x^l\, k_n(\beta x)\, e^{-\alpha x-\gamma x^2}. \quad (36)$$

The latter two integrals can be integrated numerically to a very good precision. This approach is reasonable if one does not care about the timings of the calculations (e.g., for benchmark purposes). However, to reach a computational cost comparable with GTOs and use ECPs efficiently for large systems better procedures are required, preferably recursive. They are described in detail in the next paragraphs.

Let us begin with the first class of integrals, $\mathcal{I}_{ln}$ (we drop the parentheses from now on). By using the relation (S5) one arrives at

$$\mathcal{I}_{l,n-1} = \frac{2n+1}{\beta}\mathcal{I}_{l-1,n} + \mathcal{I}_{l,n+1}. \quad (37)$$

This recursion needs to be carried out in the direction of decreasing n in order to maintain the numerical stability. To start the process (37) one requires $\mathcal{I}_{lN}$ for two neighboring (large) N and $\mathcal{I}_{0n}$. We propose to evaluate both of them by inserting the power-series expansion of $i_n(x)$ around the origin into the definition (35)

$$\mathcal{I}_{ln} = \beta^n \sum_{k=0}^\infty \frac{\left(\frac{1}{2}\beta^2\right)^k}{k!\,(2n+2k+1)!!}\,\mathcal{F}^<_{n+l+2k}(\alpha,\gamma). \quad (38)$$

Since the above summation is infinite and for practical reasons needs to be truncated, it is helpful to estimate in advance how many terms are required to achieve convergence.

We first note that the rate of convergence of Eq. (38) is not significantly affected by a change of values l, α, and γ, the only important variables being β, n. The sum (38) converges faster when β decreases or n increases. Therefore, we can consider the worst-case scenario of $\mathcal{I}_{00}$ as a function of β. Making use of the relationship $\mathcal{F}_n^<(\alpha,\gamma) \leqslant \frac{1}{n+1}$, one arrives at the formal upper bound

$$\mathcal{I}_{00} \leqslant \sum_{k=0}^\infty \frac{\beta^{2k}}{(2k)!(2k+1)^2}. \quad (39)$$

One can assume that the convergence pattern of the above series is very similar to the original $\mathcal{I}_{00}$. The number of terms necessary to achieve convergence for a given β can be estimated by solving the equality $\beta^{2k} = \epsilon\,(2k)!\,(2k+1)^2$ and rounding up to the closest integer value (ϵ is the prescribed accuracy goal). We obtained numerical solutions of Eq. (39) for a finite set of β and fitted them with a linear function, giving $n_{\text{terms}} = 0.68\beta + 29.5$. This estimation is reliable for all β, but it tends to overshoot n_{terms} slightly, especially for smaller β.

The method based on the infinite summation is quite successful for small and moderate β but becomes tedious when the values of β get large. It typically occurs for stretched molecules or for extended basis sets with high exponents. To avoid laborious summations in such situations we present a large β asymptotic expansion of the functions $\mathcal{I}_{ln}$. The derivation begins by rewriting Eq. (35) as a difference of two integrals over the intervals $[0,\infty]$ and $[1,\infty]$. In the first integral one needs to exchange the variables to βx and subsequently expand the Gaussian function under the integral sign in power series. The remaining integral can be recognized as the Legendre function of the second kind Q_n by means of the analytic continuation. This finally leads to the asymptotic formula for the first part

$$\int_0^\infty x^l\, i_n(\beta x)\, e^{-\alpha x-\gamma x^2} \sim \frac{1}{\beta^{l+1}} \sum_{k=0}^\infty \left(\frac{\gamma}{\beta^2}\right)^k Q_n^{(l)}\left(\frac{\alpha}{\beta}\right), \quad (40)$$

where the subscript in Q_n denotes differentiation with respect to the main argument. Calculation of the Legendre functions and their derivatives is a standard task as has been discussed many times in the literature [133–135]. Let us pass to the second part, i.e., the integral over $[1,\infty]$. Note that in this integral (contrary to the former) the argument of the Bessel function is always large for large β. Therefore, we can use the large-argument expansion of the Bessel function given by Eq. (S7) in Supplemental Material [107]. This straightforwardly leads to the formula

$$\int_1^\infty x^l\, i_n(\beta x)\, e^{-\alpha x-\gamma x^2} \sim \frac{1}{2}\sum_{k=0}^\infty \frac{a_{kn}}{\beta^{k+1}}\mathcal{F}^>_{l-k-1}(\alpha,\gamma). \quad (41)$$

By combining Eqs. (40) and (41) one obtains the final large-β asymptotic expansion of the integrals (35). Explicit

expressions for the coefficients in the above expression are given in Supplemental Material [107].

Passing to the second class of integrals, $\mathcal{K}_{ln}$, and inserting the explicit formula for $k_n(z)$, Eq. (S3), leads to

$$\mathcal{K}_{ln} = \frac{\pi}{2\beta} \sum_{k=0}^{n} \frac{(n+k)!}{(2\beta)^k\, k!\,(n-k)!}\, \mathcal{F}^{>}_{l-k-1}(\alpha+\beta,\gamma), \qquad (42)$$

which makes the evaluation elementary. Note that all terms in the above sum are strictly positive, so that no cancellations are possible and the final result acquires the same accuracy as the supplied values of $F_l^{>}$.

C. Spin-averaged potentials, I_{bab} type

In the case of I_{bab} configuration there are no simplifications analogous as in Eq. (26) and we must use Eqs. (24) and (25) as they stand. Therefore, the local and nonlocal parts need to be treated separately in this case. Considering the local part, note that in Eq. (24) both STOs occupy the same center. Therefore, one can expand the product of two STOs into a linear combination of STOs by using standard relations for coupling of the angular momenta. As a result, the integrals $I^{\mathrm{loc}}_{\mathrm{bab}}$ can easily be expressed in terms of

$$\begin{aligned}
&\int d\mathbf{r}\, r_b^{n_{ab}-1} e^{-\beta_{ab} r_b}\, Y_{l_{ab},0}(\theta_b,\phi_b)\, U^a_L(r_a) \\
&\quad = (-1)^{l_{ab}} \frac{2l_{ab}+1}{\sqrt{\pi}} \sum_{\lambda}^{l_{ab}} \begin{pmatrix} \lambda & l_{ab}-\lambda & l_{ab} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 2l_{ab} \\ 2\lambda \end{pmatrix}^{1/2} \\
&\qquad \times (-R)^{l_{ab}-\lambda} \sum_k A^a_{kl}\, W_{\lambda+n_{kl},n_{ab}-\lambda,\lambda}\big(0,\beta_{ab},B^a_{kl};R\big), \qquad (43)
\end{aligned}$$

where we have made use of Eq. (8) and integrated over the angles. In the above expression a handful of quantities has been introduced, i.e., $n_{ab} = n_a + n_b - 1$, $\beta_{ab} = \beta_a + \beta_b$, and $|l_a - l_b| \leqslant l_{ab} \leqslant l_a + l_b$ (note that $n_{ab} > l_{ab}$).

The remaining one-dimensional integrals in Eq. (43) are of the same class as defined by Eq. (30) but with $\alpha = 0$. Theoretically, this brings a degree of simplification and allows for a more robust scheme. However, we found that it is not worth increasing the size and complexity of the code by including separate routines for the case $\alpha = 0$. Therefore, we recommend that the case $\alpha = 0$ is treated with general techniques described above. There are no singularities or numerical instabilities in these expressions as α approaches zero, so that the codes can be reused with no changes.

Let us now consider the calculation of the nonlocal term, $I^{\mathrm{nloc}}_{\mathrm{bab}}$. This case is much more troublesome due to the fact that the coupling of the angular momenta cannot be used before the translation of the orbitals. Therefore, both STOs need to be shifted independently from the center b to the center a. After some algebra one finds

$$I^{\mathrm{nloc}}_{\mathrm{bab}} = (-1)^{l_a+l_b} \frac{(2l_a+1)(2l_b+1)}{4} \sum_{K=0}^{L-1} (2K+1)\, \mathcal{A}_K, \qquad (44)$$

where

$$\begin{aligned}
\mathcal{A}_K = &\sum_{\lambda_a}^{l_a} (-R)^{l_a-\lambda_a} \begin{pmatrix} \lambda_a & l_a-\lambda_a & l_a \\ m & 0 & -m \end{pmatrix} \begin{pmatrix} 2l_a \\ 2\lambda_a \end{pmatrix}^{\frac{1}{2}} \\
&\times \sum_{k_a} (2k_a+1) \begin{pmatrix} K & k_a & \lambda_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K & k_a & \lambda_a \\ -m & 0 & m \end{pmatrix} \mathcal{B}_{l_a m_a}
\end{aligned} \qquad (45)$$

and, analogously,

$$\begin{aligned}
\mathcal{B}_{l_a m_a} = &\sum_{\lambda_b}^{l_b} (-R)^{l_b-\lambda_b} \begin{pmatrix} \lambda_b & l_b-\lambda_b & l_b \\ m & 0 & -m \end{pmatrix} \begin{pmatrix} 2l_b \\ 2\lambda_b \end{pmatrix}^{\frac{1}{2}} \\
&\times \sum_{k_b} (2k_b+1) \begin{pmatrix} K & k_b & \lambda_b \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} K & k_b & \lambda_b \\ -m & 0 & m \end{pmatrix} \\
&\times \sum_p A^a_{pL}\, U^{n_a-l_a,n_b-l_b}_{\lambda_a+\lambda_b+n_{pL},k_a,k_b}\big(\beta_b,\beta'_b,B^a_{pL};R\big). \qquad (46)
\end{aligned}$$

Finally, the innermost integral can be expressed as

$$\begin{aligned}
&U^{m_1m_2}_{l\,n_1n_2}(\beta_1,\beta_2,\gamma;R) \\
&\quad = \int_0^\infty dr\, r^l\, \zeta_{m_1n_1}(\beta_1,r;R)\, \zeta_{m_2n_2}(\beta_2,r;R) e^{-\gamma r^2}, \qquad (47)
\end{aligned}$$

reducing all matrix elements to a definite one-dimensional integration. Let us note at this point that the integrals Eq. (47) are invariant with respect to permutation $1 \leftrightarrow 2$ of all indices (including the nonlinear parameters), i.e., $U^{m_1m_2}_{l\,n_1n_2}(\beta_1,\beta_2,\gamma;R) = U^{m_2m_1}_{l\,n_2n_1}(\beta_2,\beta_1,\gamma;R)$.

Clearly, the integrals $U^{m_1m_2}_{l\,n_1n_2}$ are the most complicated quantities appearing in the theory. Since they are five-index objects, any numerical integration is expected to be prohibitively expensive. Therefore, the recursive techniques are preferred despite the necessity to operate in many dimensions. Derivation of the recursive formulas for the basic integrals $U^{m_1m_2}_{l\,n_1n_2}$ follows along a line similar as in the previous subsection. Let us insert Eqs. (4) and (5) into the definition of $U^{m_1m_2}_{l\,n_1n_2}$. After some rearrangements one obtains

$$\begin{aligned}
U^{m_1+2,m_2}_{l\,n_1n_2} = &U^{m_1m_2}_{l+2,n_1n_2} + R^2\, U^{m_1m_2}_{l\,n_1n_2} - \frac{2R}{2n_1+1} \\
&\times \big[n_1\, U^{m_1m_2}_{l\,n_1-1,n_2} + (n_1+1)\, U^{m_1m_2}_{l\,n_1+1,n_2}\big] \qquad (48)
\end{aligned}$$

and

$$U^{1,m_2}_{l\,n_1n_2} = \frac{\beta_1 R}{2n_1+1}\big[U^{0,m_2}_{l+1,n_1-1,n_2} - U^{0,m_2}_{l+1,n_1+1,n_2}\big]. \qquad (49)$$

The exceptions from the above relation are the integrals with $n_1 = 0$ which have to be calculated according to Eq. (6) instead:

$$\begin{aligned}
U^{1,m_2}_{l\,0,n_2} = &\beta_1 R\big[U^{0,m_2}_{l+1,0,n_2} - U^{0,m_2}_{l+1,1,n_2}\big] \\
&+ e^{-\beta_1 R}\, W_{l,m_2,n_2}(\beta_1,\beta_2,\gamma;R). \qquad (50)
\end{aligned}$$

The recursion relations which allow one to increase the second pair of indices can be obtained by using the aforementioned symmetry property.

The above relations allow one to calculate $U^{m_1m_2}_{l\,n_1n_2}$ with nonzero m_1, m_2 starting solely with the integrals $U^{00}_{l\,n_1n_2}$. The

latter obey the relationship

$$U^{00}_{l\,n_1n_2} = \frac{4\beta_1\beta_2}{\pi^2} R^{l+1} \times \left[k_{n_1}(\beta_1 R)\, k_{n_2}(\beta_2 R)\, J^l_{n_1n_2}(\beta_1 R,\beta_2 R,\gamma R^2) + i_{n_1}(\beta_1 R)\, i_{n_2}(\beta_2 R)\, M^l_{n_1n_2}(\beta_1 R,\beta_2 R,\gamma R^2)\right], \quad (51)$$

where

$$\mathcal{J}^l_{n_1n_2}(\beta_1,\beta_2,\gamma) = \int_0^1 dx\, x^l\, i_{n_1}(\beta_1 x)\, i_{n_2}(\beta_2 x)\, e^{-\gamma x^2}, \quad (52)$$

$$\mathcal{K}^l_{n_1n_2}(\beta_1,\beta_2,\gamma) = \int_1^\infty dx\, x^l\, k_{n_1}(\beta_1 x)\, k_{n_2}(\beta_2 x)\, e^{-\gamma x^2}, \quad (53)$$

which results directly from Eqs. (4)–(7). Let us note that some of the indices of $U^{m_1m_2}_{l\,n_1n_2}$ must be increased only a few times at most. In fact, the maximal value of 6 for the indices n_1, n_2 is sufficient to cover the whole known Periodic Table. Moreover, in accurate calculations with Slater-type orbitals for light systems [51] one typically uses even-tempered sequences of functions with $n = l + 1$. This reduces the necessary values of n_1, n_2 to 1. A similar observation is valid for the W_{lmn} integrals defined in the previous section, Eq. (30).

Evaluation of the integrals (52) and (53) follows a very similar strategy as adopted previously. By using the power-series expansion of $i_n(z)$ one easily arrives at

$$\mathcal{J}^l_{n_1n_2} = \beta_1^{n_1} \sum_{k=0}^{\infty} \frac{\left(\beta_1^2/2\right)^k}{k!\,(2n_1+2k+1)!!}\, \mathcal{I}_{2k+l+n_1,n_2}(0,\beta_2,\gamma). \quad (54)$$

The corresponding expression involving the second pair of indices is obtained by using the symmetry relation $\mathcal{J}^l_{n_1n_2}(\beta_1,\beta_2,\gamma) = \mathcal{J}^l_{n_2n_1}(\beta_2,\beta_1,\gamma)$. Both these formulas are useful for small or moderate β_1 or β_2, but fail otherwise due to slow convergence of the infinite series. In this case one needs the large β_1 or β_2 asymptotic expansion which can be derived analogously as Eqs. (40) and (41).

Finally, evaluation of the second class of integrals $\mathcal{K}^l_{n_1n_2}$ relies on the explicit expression for the modified Bessel functions, Eq. (S3). By inserting it twice into the definition (53) and rearranging one obtains

$$\mathcal{K}^l_{n_1n_2} = \frac{\pi^2}{4\beta_1\beta_2} \sum_{k_1=0}^{n_1}\sum_{k_2=0}^{n_2} \frac{(n_1+k_1)!}{(2\beta_1)^{k_1}\,k_1!\,(n_1-k_1)!} \times \frac{(n_2+k_2)!}{(2\beta_2)^{k_2}\,k_2!\,(n_2-k_2)!}\, \mathcal{F}^{>}_{l-k_1-k_2-2}(\beta_1+\beta_2,\gamma). \quad (55)$$

D. Spin-orbit potentials

The effective spin-orbit potentials are of very similar form as the scalar pseudopotentials. In fact, they differ only due to presence of the angular momentum and spin operators, Eq. (11). Additionally, there is no local part in the spin-orbit pseudopotentials. After some manipulations one can show that the necessary matrix elements,

$$I^{\rm so}_{\rm bca} = \left\langle \chi_{n_bl_bm_b}(\mathbf{r}_b;\beta_b)\right|\hat{U}^c_{\rm PP,so}(r_c)\left|\chi_{n_al_am_a}(\mathbf{r}_a;\beta_a)\right\rangle, \quad (56)$$

can be rewritten without a loss of generality as

$$I^{\rm so}_{\rm bca} = \sum_{l=0}^{L-1}\sum_{mm'=-l}^{+l} \frac{2\,i^{-1}}{2l+1} \int_0^\infty dr_c\, r_c^2\, \Delta U^c_l(r_c) \times \left\langle \chi_{n_bl_bm_b}(\mathbf{r}_b;\beta_b)|lm\right\rangle_c \cdot {}_c\langle lm|\,\mathbf{l}_c\cdot\mathbf{s}\,|lm'\rangle_c \times {}_c\left\langle lm'|\chi_{n_al_am_a}(\mathbf{r}_a;\beta_a)\right\rangle. \quad (57)$$

To derive this expression one uses the fact that the projection operators ${}_c\langle lm|$ are idempotent and that they commute with the spin-orbit operator. The imaginary unit has been added to make all matrix elements real as the orbital angular momentum operator is, in general, complex valued. The only new objects present in Eq. (57) are matrix elements of the angular momentum operator, $\langle lm|\,\mathbf{l}\cdot\mathbf{s}\,|lm'\rangle$. Explicit expressions for these integrals can be derived with standard algebra of the angular momentum (see Ref. [108], pp. 793).

Standard quantum chemistry packages compute all basic matrix elements over spatial orbitals and the spin component is added later by proper construction of an approximate wave function. This is the approach we adopt here. The integrals (56) and (57) are evaluated for all Cartesian components separately and stored for further manipulations.

IV. CORE POLARIZATION MATRIX ELEMENTS

In order to evaluate the core polarization correction to the Hamiltonian, Eqs. (13)–(16), only two distinct matrix elements are necessary. They read

$$I^{{\rm CPP}(i)}_{\rm bca} = \left\langle \chi_{n_bl_bm_b}(\mathbf{r}_b;\beta_b)\right|\hat{V}^{(i)}_{\rm CPP}(r_c)\left|\chi_{n_al_am_a}(\mathbf{r}_a;\beta_a)\right\rangle, \quad (58)$$

with $i = 1,2$, and

$$\hat{V}^{(1)}_{\rm CPP}(r) = \sqrt{\frac{4\pi}{3}}\,\frac{Y_{1M}(\hat{r})}{r^2}\,(1-e^{-\delta r^2})^n, \quad (59)$$

$$\hat{V}^{(2)}_{\rm CPP}(r) = \frac{1}{r^4}\,(1-e^{-\delta r^2})^{2n}. \quad (60)$$

The Gaussian factors in these definitions come from the adopted cutoff function, Eq. (17). Note that instead of Cartesian coordinates in Eq. (59) we use pure spherical components corresponding to $M = -1,0,+1$. The total contribution to the Hamiltonian can be assembled by combining these matrix elements with geometric and molecular data according to Eqs. (13)–(16).

Starting with the atomic-type integrals, one can straightforwardly integrate over the angles in the spherical coordinate system, giving after some rearrangements

$$I^{{\rm CPP}(1)}_{\rm aaa} = (-1)^{m'_a}\sqrt{(2l_a+1)(2l'_a+1)}\begin{pmatrix} l'_a & 1 & l_a \\ 0 & 0 & 0\end{pmatrix} \times \begin{pmatrix} l'_a & 1 & l_a \\ -m'_a & M & m_a\end{pmatrix} \times \sum_{k=0}^{n}\binom{n}{k}(-1)^k\,\mathcal{F}^0_{n_a+n'_a-2}(\beta_a+\beta'_a,\delta), \quad (61)$$

provided that $m'_a = m_a + M$ (otherwise the result vanishes). The form of the expression for the matrix element involving

$\hat{V}^{(2)}_{\rm CPP}(r)$ depends on the value of $n_a + n'_a$. It reads

$$I^{\rm CPP(2)}_{\rm aaa} = \sum_{k=0}^{2n} \binom{2n}{k} (-1)^k \, \mathcal{F}^0_{n_a+n'_a-4}(\beta_a + \beta'_a, k\delta), \qquad (62)$$

for $n_a + n'_a \geqslant 4$,

$$I^{\rm CPP(2)}_{\rm aaa} = (\beta_a + \beta'_a) \sum_{k=0}^{2n} \binom{2n}{k} (-1)^k \, \mathcal{G}^0_0(\beta_a + \beta'_a, k\delta) + 4\delta n \sum_{k=1}^{2n-1} \binom{2n-1}{k-1} (-1)^k \, \mathcal{G}^0_1(\beta_a + \beta'_a, k\delta), \qquad (63)$$

$$I^{\rm CPP(2)}_{\rm aaa} = -(\beta_a + \beta'_a) \times \text{the above} - 4\delta n \sum_{k=1}^{2n} \binom{2n-1}{k-1} (-1)^k \, \mathcal{F}^0_0(\beta_a + \beta'_a, k\delta), \qquad (64)$$

for $n_a + n'_a = 3$ and $n_a + n'_a = 2$, respectively. Let us recall that the above matrix elements are nonzero if and only if $l_a = l'_a$ and $m_a = m'_a$.

Passing to the two-center matrix elements, we first note that calculation of $I^{\rm CPP(1)}_{\rm baa}$ and $I^{\rm CPP(1)}_{\rm bab}$ is almost exactly the same as for the local components of the spin-averaged potentials described in Secs. III B and III C. Thus there is no need to repeat the details of the derivation and we provide only a short sketch for convenience of the reader. Considering $I^{\rm CPP(1)}_{\rm baa}$, the major difference as compared with the derivation given in Sec. III B is that two spherical harmonics placed on the center a need to be coupled first. Next, translation of the STO from the center b to the center a enables one to integrate over the angles and the Jacobian cancels the apparent $1/r^2$ singularity introduced by the potential (59). This allows one to expand the Gaussian damping function with help of the binomial theorem and the final result is written as a linear combination of the W_{lmn} integrals defined by Eq. (30). A similar conclusion is found for the $I^{\rm CPP(1)}_{\rm bab}$ integrals class. Two STOs present on the center a need to be expanded into a linear combination of STOs giving an analog of Eq. (43). Once we translate the distribution from center b to center a and integrate over the angles, the singularity vanishes and the rest of the derivation is straightforward. The final result can also be written in terms of the integrals (30).

Unfortunately, calculation of the matrix elements involving the potential $\hat{V}^{(2)}_{\rm CPP}(r)$ is more involved. This is due to the fact that the apparent singularity is not automatically canceled by the Jacobian and thus the damping factor in Eq. (60) cannot be expanded that easily. As a result, in addition to the ordinary integrals introduced in Secs. III B and III C one requires

$$\widetilde{\mathcal{I}}^p_{ln}(\alpha,\beta,\delta) = \int_0^1 dx \, x^l \, i_n(\beta x) \, e^{-\alpha x} \, (1 - e^{-\gamma x^2})^p, \qquad (65)$$

$$\widetilde{\mathcal{K}}^p_{ln}(\alpha,\beta,\delta) = \int_1^\infty dx \, x^l \, k_n(\beta x) \, e^{-\alpha x} \, (1 - e^{-\gamma x^2})^p, \qquad (66)$$

where the analogy with Eqs. (35) and (36) is obvious. However, the values of l are not restricted to nonnegative integers here since $l = -1, -2$ are also necessary. For the integrals $\widetilde{\mathcal{K}}^p_{ln}$ this is not problematic because of the integration range. Only the integrals $\widetilde{\mathcal{I}}^p_{-1,n}$ and $\widetilde{\mathcal{I}}^p_{-2,n}$ are troublesome. To bring them into a closed form we introduce the following quantities:

$$\mathcal{M}_{ln}(\alpha,\beta,\gamma) = \int_0^1 dx \, x^l \, \ln x \, i_n(\beta x) \, e^{-\alpha x - \gamma x^2}, \qquad (67)$$

so that $\widetilde{\mathcal{I}}^p_{-1,n}$ and $\widetilde{\mathcal{I}}^p_{-2,n}$ can now be simplified by integration by parts. This gives

$$\begin{aligned} \widetilde{\mathcal{I}}^p_{-1,n}(\alpha,\beta,\delta) &= -\frac{n\beta}{2n+1} \sum_{k=0}^{p} \binom{p}{k} (-1)^k \mathcal{M}_{0,n-1}(\alpha,\beta,k\delta) \\ &\quad - \frac{\beta(n+1)}{2n+1} \sum_{k=0}^{p} \binom{p}{k} (-1)^k \mathcal{M}_{0,n+1}(\alpha,\beta,k\delta) \\ &\quad + \alpha \sum_{k=0}^{p} \binom{p}{k} (-1)^k \mathcal{M}_{0,n}(\alpha,\beta,k\delta) \\ &\quad + 4p\delta \sum_{k=1}^{p} \binom{p-1}{k-1} (-1)^k \mathcal{M}_{1,n}(\alpha,\beta,k\delta) \end{aligned} \qquad (68)$$

and

$$\begin{aligned} \widetilde{\mathcal{I}}^p_{-2,n} &= \frac{\beta n}{2n+1} \widetilde{\mathcal{I}}^p_{-1,n-1} + \frac{\beta(n+1)}{2n+1} \widetilde{\mathcal{I}}^p_{-1,n+1} \\ &\quad - \alpha \, \widetilde{\mathcal{I}}^p_{-1,n} - 4p\delta \, \widetilde{\mathcal{I}}^p_{0,n} + 4p\delta \, \widetilde{\mathcal{I}}^{p-1}_{0,n}, \end{aligned} \qquad (69)$$

where the notation for the nonlinear parameters (α,β,γ) has been suppressed when it is clear from the context. Finally, calculation of the integrals $\mathcal{M}_{ln}$ is reminiscent of the methods introduced in Sec. III B. For example, for small and moderate β

$$\mathcal{M}_{ln}(\alpha,\beta,\gamma) = \beta^n \sum_{k=0}^{\infty} \frac{\left(\frac{1}{2}\beta^2\right)^k}{k! \, (2n+2k+1)!!} \, \mathcal{G}^<_{n+l+2k}(\alpha,\gamma). \qquad (70)$$

This finalizes the present section of the paper.

V. NUMERICAL EXAMPLES

Throughout the paper we use atomic units for calculated quantities unless explicitly stated otherwise. The approximate conversion factors are $1a_0 = 0.52\,917$ Å for lengths (Bohr radius), 1 a.u. = 219 474.63 cm^{-1} for energies, and 1 a.u. = 2.54 158 Debye (D) for dipole moments.

A. Basis set optimization

While there are many families of pseudopotentials available in the literature, the same cannot be said about the relevant Slater-type basis sets. Therefore, we performed optimization of the valence STOs basis sets for three elements—calcium, strontium, and barium (Ca, Sr, and Ba). The last known element of the rare-earth metals (radium, Ra) is not considered here because it is highly radioactive and thus not enough confirmed experimental data is available to constitute a comprehensive test case. For all elements we adopted the Stuttgart-Dresden family of energy consistent pseudopotentials. The so-called

small-core pseudopotentials (10 valence electrons) are described in Ref. [136], whilst the large-core counterparts (two valence electrons) are given in Ref. [137].

In general, construction of the STOs basis sets for pseudopotential calculations is similar as in the recent paper concerning the beryllium dimer [51]. Therefore, we shall not repeat the minutiae of the procedure and illuminate only the most important differences. First, instead of the conventional even-tempered stencil for the nonlinear parameters (exponents) of each angular momentum we use the following extended scheme (well tempering):

$$\zeta_{il} = \alpha_l \cdot \beta_l^{\,i\,(1+\gamma_l i+\delta_l i^2)}, \tag{71}$$

where $i = 0, \ldots, n_l$, l is the angular momentum, and $\alpha_l, \beta_l, \gamma_l, \delta_l$ are variational parameters optimized for each l. For $l > 2$ we set $\delta_l = 0$ to reduce the number of parameters. The second difference is the choice of the target function—total atomic valence correlation energy, i.e., we do not freeze any additional orbitals in the valence space. Let us mention that there are many similarities between the basis set optimization procedures in the all-electron systems and for the valence-only pseudopotential. However, the latter case is much more technically challenging. This is mainly due to occurrence of numerous local minima and problematic behavior of the pseudo-orbitals near the nucleus causing the linear dependencies problem.

The basis sets optimized in the course of the present work are constructed according to the correlation consistency principle [138]. They are abbreviated wtcc-l (well-tempered correlation-consistent), where l is the highest angular momentum present in the basis set. For example, for the valence-only ten electron systems (small-core pseudpotentials) the smallest basis set (wtcc-2) has composition $10s8p3d$ and the largest (wtcc-5) has $13s11p7d5f4g2h$. This includes two sets of additional diffuse functions which were trained to maximize the atomic polarizability calculated at the closed-shell Hartree-Fock level. All basis sets used in this work can be obtained from the authors upon request.

B. Test results

In order to check the accuracy of the new basis sets and correctness of the procedures given in this work we performed extensive numerical tests. For each atom (Ca, Sr, and Ba) we evaluated the first three excitation energies and the first ionization potential (IP). The results are given in Tables I–III. Additionally, in Tables IV and V we provide ground-state dipole polarizabilities (static) and outermost ns valence orbitals Hartree-Fock energies, respectively. All calculations were performed both with large- and small-core pseudopotentials (2 and 10 valence electrons, respectively). In the case of the large-core pseudopotentials the corresponding core polarization potential was included by default. All valence two-electron calculations were performed with the CCSD method [145] and its variants for the excited and ionized states (EOM, IP-EOM [146–148]).

For the 10 electron systems (small-core pseudopotentials) the calculations are slightly more involved. For the excited states we used the EOM-CC3 method [149] as implemented in the code for excited-state properties of Tucholska *et al.* [150,151] with all orbitals active. For the ionized states we used the IP-EOM2 method [152], and the polarizabilities were evaluated at the CCSD and CCSD(T) [153] levels by using a two-point finite difference method with displacement of 10^{-4} a.u. All calculations were performed with the help of locally modified versions of the GAMESS [154,155] and ACESII [156] program packages, with an exception of the computations at the CC3 level of theory where we used a program written by one of us (A.M.T.). In all calculations presented in this section the largest basis sets available in each case are used—wtcc-5 for the small-core pseudopotentials and wtcc-3 for the large-core counterparts.

Let us begin the analysis with the atomic excitation spectra and consider the strontium atom as an example. The overall picture is more or less the same for the remaining atoms and we shall comment on the differences further in the text. One can see that both the small-core and large-core pseudopotentials give a very good agreement with the experimental data. However, the small-core pseudopotential combined with the

TABLE I. Results of the calculations for the calcium atom (see the main text for technical details). The abbreviation IP stands for first ionization potential of the system. Small-core PP subtracts 10 electrons from the system (ECP10MDF) while large-core PP subtracts 18 electrons (ECP18SDF). All values are given in wave numbers, cm^{-1}.

	Large-core PP	Small-core PP		
State	CCSD	CCSD	CC3	Expt.[a]
^{3}P	15097.0	15173.2	15195.3	15263.1
^{3}D	20941.1	20856.1	21299.6	20356.6
^{1}D	22216.8	22878.6	22859.0	21849.6
^{1}P	23429.8	24845.8	23879.6	23652.3
^{3}S	31651.2	31828.7	31545.5	31539.5
^{1}S	33411.0	33890.9	33336.9	33317.3
IP	49405.2	49821.9		49305.9

[a]Experimental values taken from Refs. [139,140]; the experimental values for the triplet states deduced from the Landé rule.

TABLE II. Results of the calculations for the strontium atom (see the main text for technical details). The abbreviation IP stands for first ionization potential of the system. Small-core PP subtracts 28 electrons from the system (ECP28MDF) while large-core PP subtracts 36 electrons (ECP36SDF). All values are given in wave numbers, cm^{-1}.

	Large-core PP	Small-core PP		
State	CCSD	CCSD	CC3	Expt.[a]
^{3}P	14579.9	14546.3	14597.2	14702.9
^{3}D	18442.2	18155.0	18393.7	18253.8
^{1}D	20380.4	20584.7	20411.1	20149.7
^{1}P	21451.1	22701.9	21797.5	21698.5
^{3}S	29201.4	29189.7	28939.3	29038.8
^{1}S	30634.4	31063.1	30508.6	30591.8
IP	46006.2	46284.4		45932.2

[a]Experimental values taken from Refs. [141,142]; the experimental values for the triplet states deduced from the Landé rule.

TABLE III. Results of the calculations for the barium atom (see the main text for technical details). The abbreviation IP stands for first ionization potential of the system. Small-core PP subtracts 46 electrons from the system (ECP46MDF) while large-core PP subtracts 54 electrons (ECP54SDF). All values are given in wave numbers, cm^{-1}.

State	Large-core PP CCSD	Small-core PP CCSD	Small-core PP CC3	Expt.[a]
^{3}D	9419.4	8923.7	9178.1	9357.8
^{1}D	11609.6	11653.5	11391.4	11395.5
^{3}P	12986.2	12823.6	12925.9	13085.5
^{1}P	17578.9	19527.3	18284.6	18060.3
^{3}S	26281.3	26269.3	26141.9	26160.3
^{1}S	27275.0	[b]	[b]	26757.3
IP	42156.4	42245.8		42034.9

[a]Experimental values taken from Refs. [143,144]; the experimental values for the triplet states deduced from the Landé rule.
[b]EOM iterations failed to converge.

CC3 method performs better, as could have been expected. The average deviation from the experimental data is around 0.6% for the small-core and 0.9% for the large-core potentials. One can safely say that the ECP-MDF/CC3 level of theory is very reliable. On average, excitation energies are expected to be less than 1% away from the experimental data. Additionally, no significant increase of the error is observed for any particular spatial symmetry or spin state. This suggests that the new basis sets have no inherent bias, which is a desirable feature in a molecular work.

Excitation energies for barium are in only slightly worse agreement with the experiment than in the case of strontium. The average error is around 0.9% for the small-core and 1.7% for the large-core pseudopotentials. Unfortunately, we observe a significant error for the ^{3}D and ^{1}D states of calcium with both pseudopotentials. This behavior is surprising because the remaining excitation energies are in good agreement with the experiment. Therefore, our first suspicion was that ^{3}D and ^{1}D states are highly diffused and the basis set is not saturated well enough. However, we found that further extension of the basis set changed the results by less that 100 cm^{-1}, which is not enough to explain the discrepancy. As a result, we presume that this increase in the error is an inherent problem of the given pseudopotentials. We note that in the original papers describing the pseudopotentials [136,137] errors obtained for Ca were in fact significantly larger than for the other elements.

TABLE IV. Dipole polarizabilities of the ground state of the calcium, strontium, and barium atoms. All values are given in the atomic units.

Atom	Theory	Large-core PP	Small-core PP	Expt.
	HF	164.50	181.60	
Ca	CCSD	170.38	159.14	169 ± 17[a]
	CCSD(T)		156.12	
	HF	205.14	231.94	
Sr	CCSD	221.48	203.16	186 ± 15[b]
	CCSD(T)		198.52	
	HF	280.36	327.48	
Ba	CCSD	323.48	284.70	268 ± 22[c]
	CCSD(T)		276.62	

[a]References [157,158].
[b]Reference [159].
[c]Reference [157].

TABLE V. Outermost valence orbital energies calculated with the pseudopotentials compared with the reference all-electron Dirac Hartree Fock (DHF). All values have their signs reversed and are given in the atomic units.

Atom	Shell	Large-core PP	Small-core PP	All-electron DHF[a]
Ca	4*s*	0.2064	0.1967	0.1963
Sr	5*s*	0.1930	0.1813	0.1813
Ba	6*s*	0.1760	0.1630	0.1632

[a]Taken from Ref. [136].

Let us also compare our results for the strontium atom with the values obtained by Skomorowski *et al.* [57]. In this work the same pseudopotential (ECP28MDF) was used in combination with a custom-made GTOs basis set and the EOM-CC3 method. Both basis sets are roughly of the same size, so a fair comparison is possible. Skomorowski *et al.* [57] give 14570.8 cm^{-1} and 21764.3 cm^{-1} for the nonrelativistic ^{3}P and ^{1}P states, respectively. These results are very similar to the values given in Table II; any differences are probably accidental, suggesting that both basis sets are of a similar quality for the *P* states. However, the situation is different for the D states. The authors of Ref. [57] report 18668.8 cm^{-1} for the ^{3}D state and 20650.3 cm^{-1} for the ^{1}D state. Clearly, errors with respect to the experimental values are much larger than for the P states, and also by few hundreds cm^{-1} larger than calculated with our basis sets (cf. Table II).

Next, we would like to check the quality of the basis sets for properties different than the atomic spectra. First, let us consider the static dipole polarizabilities calculated with both families of pseudopotentials. The results are given in Table IV. The large-core pseudopotentials underperform considerably—the calculated values differ by more than 10% from the experimentally determined ones (and lie outside the corresponding error bars). The only exception is the calcium atom, but this agreement is probably accidental. A completely different picture is found for the small-core pseudopotentials. Here, calculated values are reasonably close to the experiment and lie within the given error bars. We estimate the basis set error to be smaller than 1 a.u. by observing the effect of additional diffuse functions. Omission of the higher cluster operators brings an uncertainty of 1–2 a.u. assuming that the results converge geometrically with the excitation level. Therefore, one can expect that the theoretical limits are 2–3 a.u. below the values given in Table IV. This is still slightly above the experiment for Sr and Ba and somewhat below for Ca. The remaining discrepancy might be a result of an inherent pseudopotential error or a systematic error in the experimental data.

Lastly, we would like to consider the outermost valence *ns* orbital energies calculated with the pseudopotentials and compare them with all-electron Dirac-Hartree-Fock (DHF) values which we treat as a reference. Note that this quantity is very

important for chemical bonding phenomena and it is connected with some important descriptors such as the electronegativity, etc. The results are given in Table V. Remarkably, the small core pseudopotentials reproduce 3–4 significant digits for all atoms. The large-core counterparts are not that accurate and overestimate the energy by 5%–10%. This alone allows one to predict that small-core pseudopotentials are expected to be much more reliable in molecular studies.

C. Results for diatomic systems

To keep the length of the paper within reasonable limits we concentrate here on two molecules—strontium hydride and barium hydride (SrH and BaH). Both of them have attracted significant attention recently [74,161–164]. We present results obtained with the more reliable small-core pseudopotentials only. Analogous results for the large-core effective potentials can be obtained from the authors upon request.

For each of the molecules we evaluate the interaction energy (D_e) of the ground $X\,^2\Sigma^+$ state at the experimentally determined geometry. We set the interatomic distance to $R = 2.1461$ and $R = 2.2319$ for SrH and BaH, respectively, in accordance with the most recent experimental studies [165,166]. Additionally, we evaluate the permanent dipole moment of both molecules and their vertical ionization energy.

The procedure for evaluation of the aforementioned quantities is as follows. The interaction energy (i.e., the well depth) is evaluated at the all-electron CCSD(T) level of theory by using the new basis sets, wtcc-l, with $l = 2,3,4,5$. Next, valence full triples correction is added, obtained at a difference between the frozen-core full CI (FCI) and frozen-core CCSD(T) values. All results are extrapolated towards the complete basis set by using the ordinary L^{-3} formula. The ionization energy is evaluated as a difference between the extrapolated CCSD(T) energies of the molecule and the corresponding ion at a fixed geometry. Permanent dipole moments of the molecules are evaluated with the finite field method by using displaced CCSD(T) energies. In contrast to the other quantities, basis set convergence pattern for the dipole moment is not entirely regular. Thus the extrapolation to the complete basis set has not been attempted and we simply give values calculated with the largest available basis sets.

Let us begin the analysis with the interaction energy of the barium hydride. This quantity is interesting because of a controversy connected with interpretation of the experimental data. The original experimental work of Kopp *et al.* [160] gives the value $D_e < 16350.0$ cm^{-1}. However, in a recent paper of Moore *et al.* [74] a significantly larger value has been obtained from *ab initio* calculations, $D_e = 16895.12$ cm^{-1}. The discrepancy can be explained by assuming that the asymptote of one of the electronic states has been incorrectly identified. By selecting the correct Ba($^3D_3$) asymptote instead of Ba($^3D_1$), a revised experimental value is obtained, $D_e < 16910.6$ cm^{-1}. Our *ab initio* results are given in Table VI and the final value, $D_e = 16901.5$ cm^{-1}, supports the revision of the experimental data. The difference between the theoretical value and the original experimental result ($\approx$550 cm^{-1}) is too large to be explained by the basis set error or the pseudopotential error. Moreover, the agreement between our result and the value of Moore *et al.* [74] is striking. Note that the Δfci correction is very small for this molecule, of the order of a few wave numbers, indicating that the CCSD(T) method works exceptionally well for this molecule.

TABLE VI. Dissociation energy of the barium hydride (see the main text for technical details) calculated with small-core pseudopotential (ECP46MDF). The abbreviations "ae" and "fc" stand for all electron and frozen core, respectively. The quantity in the last column (Δfci) is the difference between the dissociation energies calculated at the frozen-core FCI and CCSD(T) levels. The row denoted ∞ lists values extrapolated to the complete basis set. All values are given in wave numbers, cm^{-1}.

Basis	ae-CCSD(T)	fc-CCSD(T)	Δfci	Total
wtcc-2	13249.6	14239.9	+4.6	13254.2
wtcc-3	15701.2	15975.0	+0.3	15701.5
wtcc-4	16393.9	16355.8	−1.2	16392.7
wtcc-5	16645.7	16411.9	−1.9	16643.8
∞	16903.9	16563.8	−2.4	**16901.5**
Expt.[a]				<16350.0
Rev. expt.[b]				<16910.6

[a]The original experimental value of Kopp *et al.* [160].
[b]Revision of the experimental value, Moore *et al.* [76].

Passing to the second molecule, strontium hydride, the corresponding results are given in Table VII. Unfortunately, for this system we have no direct experimental results at our disposal. However, we can compare our results with values reported in other theoretical papers. The most recent result of Liu *et al.* [164] gives $D_e = 14114.6$ cm^{-1}, i.e., differing merely by 17 cm^{-1} or about 0.1%. The somewhat older paper of Gao *et al.* [163] gives $D_e = 14259.8$ cm^{-1}—a slightly larger deviation from our value. However, let us note that a significantly smaller basis set was used in this work. Overall, it appears that the newest theoretical values converge towards the most probable result around $D_e = 14100$ cm^{-1}. Parenthetically, the values of the Δfci correction are by an order of magnitude larger for SrH than for BaH, indicating that the former possesses a much more pronounced multireference character.

TABLE VII. Dissociation energy of the strontium hydride (see the main text for technical details) calculated with small-core pseudopotential (ECP28MDF). The abbreviations "ae" and "fc" stand for all electron and frozen core, respectively. The quantity in the last column (Δfci) is the difference between the dissociation energies calculated at the frozen-core FCI and CCSD(T) levels. The row denoted ∞ lists values extrapolated to the complete basis set. All values are given in wave numbers, cm^{-1}.

Basis	ae-CCSD(T)	fc-CCSD(T)	Δfci	Total
wtcc-2	12157.2	13221.7	+28.1	12185.3
wtcc-3	13561.4	14280.3	+31.0	13592.4
wtcc-4	13881.9	14428.6	+29.2	13911.1
wtcc-5	13982.5	14474.3	+28.7	14011.2
∞	14103.9	14530.6	+28.0	**14131.9**
Other theor.				14259.8[a]
				14114.6[b]

[a]Reference [163].
[b]Reference [164].

TABLE VIII. Molecular properties of strontium and barium hydrides calculated with the small-core pseudopotentials. The abbreviations μ and IP stand for the absolute values of the permanent electronic dipole moment and the (vertical) ionization potential. IPs and dipole moments are given in units of wave numbers (cm^{-1}) and Debyes (D), respectively.

	SrH		BaH	
	ae-CCSD	ae-CCSD(T)	ae-CCSD	ae-CCSD(T)
IP	42707.5	42917.6	38453.6	38791.6
μ	13.49	13.53	14.30	14.38

Finally, in Table VIII we present vertical ionization potentials and permanent electronic dipole moments calculated for both molecules. Unfortunately, these values are not directly comparable with any experimental data available. Nonetheless, they can be used for comparison with other theoretical results, e.g., note that the permanent dipole moments of SrH reported here are substantially larger than the values given by Gao *et al.* [163].

To conclude this section we would like to comment on the computational efficiency of the procedures for calculation of the pseudopotentials matrix elements. In all applications reported here we found these quantities to be much more computationally expensive than the standard one-electron integrals, both in the atomic and diatomic systems. However, this cost is still insignificant compared to the two-electron matrix elements of the electron-electron repulsion operator. Therefore, calculations of the effective core potentials matrix elements do not constitute any significant bottleneck within the present approach.

VI. CONCLUSIONS

We have presented a general theory to evaluate matrix elements of effective core potentials in a one-electron basis set of Slater-type orbitals. As a rule, we have used the Barnett-Coulson translation method for STOs whenever possible. It generates transparent formulas and all infinite summations truncate. As a result, the matrix elements are reduced to relatively simple one-dimensional integrals. We have presented a scheme to evaluate them to a very good precision.

Next, we have shown that the matrix elements of the spin-orbit pseudopotentials are reduced to the same basis quantities as averaged effective potentials and only minor modifications are necessary to accomplish the calculations. Somewhat larger changes are necessary to facilitate computations with the core polarization potentials due to the apparent singularities in the potential. Additional one-dimensional integrals with logarithmic singularities appear and we have discussed their evaluation in detail.

Finally, various numerical examples have been provided to verify the validity of the present approach. First, we have shown a set of test results for the calcium, strontium, and barium atoms, and compared the excitation energies, dipole polarizabilities, and valence orbital energies with reliable reference (exact or experimental) data. In all cases we have found a very good agreement. Lastly, we have considered two molecular systems (strontium and barium hydrides) and evaluated interaction energies, permanent dipole moments, and ionization energies; deviations from the available experimental values have been found surprisingly small.

In this paper we have concentrated mainly on the diatomic molecules. However, the present approach can probably be extended to an arbitrary polyatomic case with relative ease. This may be important for calculations in the spirit of density functional theory [167], but also for general quantum chemical calculations for polyatomic systems in the STOs basis in the face of recent improvements in many-center STOs integrals technology [168].

The code for evaluation of matrix elements of the effective core potentials in the STOs basis described in this paper has been incorporated in the KOŁOS program: *general purpose ab initio program for electronic structure calculations with Slater-type orbitals, geminals, and Kołos-Wolniewicz functions*.

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Paper VI

"Potential energy curve for the $a^3\Sigma_u^+$ state of lithium dimer with Slater-type orbitals"

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preprint

Commentary

In Paper VI we present results of precision calculations of the full potential energy curve (PEC) for the $a^3\Sigma_u^+$ state of lithium dimer in the basis set of STOs. This is an interesting and challenging system, mostly in the context of the experimental works concerning the Bose-Einstein condensation of ultracold lithium atoms and high-resolution Fourier transform spectroscopy.

Accurate STOs basis sets for the lithium atom are developed according to the prescription laid out in Paper III. The total interaction energy of the lithium atom is divided into a set of components which are evaluated separately. The dominant contribution to the nonrelativistic Born-Oppenheimer interaction energy is evaluated with help of the CCSD(T) method. The post-CCSD(T) corrections are calculated by using the CCSDT and FCI methods in smaller basis sets. The one-electron relativistic corrections are treated perturbatively with help of the Cowan-Griffin Hamiltonian. The leading-order finite nuclear mass correction (the adiabatic correction) is calculated at the CCSD level of theory. Finally, we estimate the magnitude of the quantum electrodynamics effects (the Lamb shift).

The aforementioned *ab initio* calculations were performed at the grid of internuc-

lear distances (R) spanning from $R = 5.5$ a.u to $R = 40.0$ a.u. comprising more than 40 points. The raw theoretical data is then fitted with a suitable functional form and used to solve the nuclear Schrödinger equation. If available, we employ the near-exact long-range asymptotic coefficients calculated with more accurate theoretical methods.

In the second part of the work we use the newly developed *ab initio* potential energy curve to calculate the molecular parameters (D_e, D_0, ω_e, R_e, etc.), as well as the corresponding vibrational energy levels. In all cases we find a very good agreement with the experimental data available in the literature. For example, the total binding energy of the $^{7,7}Li_2$ isotopomer determined by us ($D_0 = 301.61\,\mathrm{cm}^{-1}$) differs by only about $0.2\,\mathrm{cm}^{-1}$ from the latest experimental result ($D_0 = 301.83\,\mathrm{cm}^{-1}$). A similarly good agreement is found for the vibrational energy levels where the average error is approximately $0.3\,\mathrm{cm}^{-1}$. Finally, we attempt to evaluate the scattering length of two lithium atoms in the ^2S ground state. Despite the value obtained by us is by a factor of three too small, we correctly predict the sign of this quantity.

To sum up, in Paper VI we have presented the most accurate theoretical calculations for the $a^3\Sigma_u^+$ state of lithium dimer available in the literature thus far. Additionally, this is probably the first work to date where a spectroscopically accurate PEC has been generated for a many-electron molecule with the help of STOs.

Potential energy curve for the $a^3\Sigma_u^+$ state of lithium dimer with Slater-type orbitals

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We report state-of-the-art *ab initio* calculations of the potential energy curve for the $a^3\Sigma_u^+$ state of the lithium dimer conducted to achieve spectroscopic accuracy ($<1\mathrm{cm}^{-1}$) without any prior adjustment to fit the corresponding experimental data. The nonrelativistic clamped-nuclei component of the interaction energy is calculated with a composite method involving six-electron coupled cluster and full configuration interaction theories combined with basis sets of Slater-type orbitals ranging in quality from double- to sextuple-zeta. To go beyond the nonrelativistic Born-Oppenheimer picture we include both the leading-order relativistic and adiabatic corrections, and find both of these effects to be non-negligible within the present accuracy standards. The potential energy curve developed by us allowed to calculate molecular parameters (D_e, D_0, ω_e etc.) for this system, as well as the corresponding vibrational energy levels, with an error of only a few tenths of a wavenumber ($0.2-0.4\,\mathrm{cm}^{-1}$). We also report an *ab initio* value for the scattering length of two ^2S lithium atoms which determines the stability of the related Bose-Einstein condensate.

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I. INTRODUCTION

Lithium dimer is one of the simplest (bound) homonuclear many-electron molecules. Therefore, it has attracted a significant attention in the past years with many experimental [1–31] and theoretical [32–38] works devoted entirely to its observation and description. However, singlet electronic states of Li_2 were the main subjects of the studies; Refs. [39–47] provide a good overview on this topic.

In contrast, the triplet electronic states of the lithium dimer have been observed for the first time only relatively recently. Experimental studies of the triplet states of Li_2 are difficult because transitions from the ground $X^1\Sigma_g^+$ state are dipole-forbidden. Moreover, the spin-orbit coupling in lithium is very weak. This impasse has been broken by improvements in experimental techniques such as perturbation-facilitated optical-optical double resonance (PFOODR) [9, 10, 19, 20]. Xie and Field [9, 10] were the first to access the triplet state $a^3\Sigma_u^+$ and determine the relevant spectroscopic constants. They started with the (bound) ground state $X^1\Sigma_g^+$ and excited into the mixed $A^1\Sigma_u^+ - b^3\Pi_u$ manifold. A subsequent fluorescence led to the final $a^3\Sigma_u^+$ state. Later, Martin et al. [23, 41], Linton et al. [12, 13], and others [17] determined accurate vibrational and rotational constants for this state by using high-resolution Fourier transform spectrometry. These data were further revised by Zemke and Stwalley [48] reporting more bound vibrational levels than initially claimed. Abraham et al. [49] performed photoassociation of ultracold lithium atoms allowing to determine precise positions of the highest vibrational levels. Finally, Linton et al. [24] determined spectroscopic constants for the $a^3\Sigma_u^+$ state to the accuracy of only a small fraction of cm^{-1}. This progress was accompanied by a number of works where semiempirical potentials were developed to reproduce the experimental spectra (see, for example, Refs. [52–55] and references therein).

Observation of the Bose-Einstein condensate of the lithium atoms [49–51] sparked a renewed interest in the $a^3\Sigma_u^+$ state. In fact, the stability of the Bose-Einstein condensate depends on the sign of the scattering length of two lithium atoms in the ground state, a. This quantity can be calculated from first principles having an accurate potential energy curve (PEC) for the $a^3\Sigma_u^+$ state. Unfortunately, the scattering length is very sensitive to tiny details of the PEC, especially in the asymptotic region. This can be illustrated by an approximate formula [56], $a^2 \approx \frac{\hbar^2}{m|E_b|}$, relating the scattering length (a) to the binding energy of the highest occupied vibrational level, E_b (m is the atomic mass). One can see that even a relatively small change in the well-depth of the PEC can shift the value of E_b significantly and thus impact the calculated scattering length dramatically. This makes accurate *ab initio* determination of a very challenging and it has been achieved thus far only for the smallest systems.

The triplet $a^3\Sigma_u^+$ state of the lithium dimer is weakly bound with the PEC well-depth of about 334 cm^{-1} and a minimum around 4.2 Å [54]. Despite that, it accommodates as many as ten vibrational levels. To get a broader picture, let us present a short survey of theoretical results available in the literature for this state.

The first works devoted to various electronic states of Li_2 employed effective core potentials (with one valence electron) and optional core polarisation corrections. The papers of Konowalow and coworkers [57–61], Müller and Mayer [62], Schmidt-Mink et al. [63], and several others [64], are prime examples of this approach. The biggest advantage of the core potentials is that the remaining effective two-electron system can be treated with relative

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ease. As a result, many excited states of different spatial and spin symmetries can be studied simultaneously, as best illustrated by recent papers of Jasik et al. [65–67]. Unfortunately, the accuracy of this effective approach is somewhat limited, with errors reaching several percents for some quantities. To reduce this error a more elaborate first-principles method must be used. This has recently been achieved by Musial and Kucharski [68] by using a sophisticated all-electron coupled cluster approach. The error has been reduced by an order of magnitude compared with the previous works; at the same time, more than thirty electronic states were characterised.

In this paper we present state-of-the-art *ab initio* PEC for the $a^3\Sigma_u^+$ state of the lithium dimer. We combine high-level quantum chemical methods with large one-electron basis sets composed of Slater-type orbitals (STOs) [69, 70] to reach saturation of the calculated values. We employ techniques for calculation of the two-centre matrix elements over STOs reported recently [71–75]. Moreover, we evaluate corrections arising from several minor physical effects, e.g., adiabatic or relativistic. We also calculate various spectroscopic parameters such as dissociation energy, vibrational energy levels etc. and compare them with the latest experimental data. We would like to emphasise that all calculations reported here utilise only rigorous *ab initio* methods. In other words, the results were obtained with no prior reference to the empirical data.

II. ELECTRONIC STRUCTURE CALCULATIONS

A. Basis sets

In accurate *ab initio* calculations employing basis sets of any kind it is of uttermost importance to generate a systematic sequence of basis sets guaranteeing that the results converge to the exact answer. This allows for reliable extrapolation towards the complete basis set (CBS) limit and (partly) overcomes the slow convergence of the correlation energy with the basis set size. Unfortunately, we are not aware of any openly available Slater-type basis sets which would satisfy the present accuracy requirements. There are many papers devoted to optimisation of the STOs basis sets in the literature [76–81]. However, they are either very old and concentrated mainly on atomic properties or aimed at the density functional theory calculations where the basis set requirements are different. As a result, the first step of this work is optimisation of Slater-type basis sets fulfilling the high accuracy standards of the present study.

All basis sets used in this paper are composed of canonical STOs [69, 70]

$$\chi_{lm}(\mathbf{r};\zeta) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}}\, r^l e^{-\zeta r}\, Y_{lm}(\theta,\phi), \qquad (1)$$

TABLE I. Composition of the STOs basis sets wtcc-l and da-wtcc-l for the lithium atom; l is the largest angular momentum included (see the main text for details).

l	atomic	diffuse
1	$5s1p$	$2s1p$
2	$6s2p1d$	$2s2p1d$
3	$7s3p2d1f$	$2s2p2d1f$
4	$8s4p3d2f1g$	$2s2p2d2f1g$
5	$9s5p4d3f2g1h$	$2s2p2d2f2g1h$
6	$10s6p5d4f3g2h1i$	$2s2p2d2f2g2h1i$

where $\zeta > 0$ is a free nonlinear parameter, and Y_{lm} are the spherical harmonics in the Condon-Shortley phase convention. By the term "canonical STOs" we mean that the power of r is equal to the angular momentum, l.

To optimise the nonlinear parameters we employ the well-tempering scheme; exponents for a given angular momentum l are written as

$$\zeta_{lk} = \alpha_l\, \beta_l^{k+\gamma_l k^2} \quad \text{with } k = 0, 1, 2, \ldots \qquad (2)$$

where α_l, β_l, and γ_l are the actual parameters which have to be determined variationally. Well-tempering (or related schemes) not only reduce the computational costs of the optimisation, but also alleviate the linear dependency problems and help to avoid troublesome local minima. The latter merit is particularly advantageous in maintaining the consistency of the basis sets sequence. At the same time, the flexibility of Eq. (2) is usually surprisingly good. Brute-force optimisations typically give only marginally better results, especially when a large number of functions are included.

When deciding on the composition of the STOs basis sets we follow the correlation-consistency principle, first proposed by Dunning [82]. The smallest basis set considered here has the composition $5s1p$ and is systematically expanded, re-optimising the nonlinear parameters at each step. This gives a sequence of basis sets denoted shortly wtcc-l (well-tempered correlation-consistent) where l is the largest angular momentum included. A detailed composition of these basis sets is given in Table I. To find the optimal values of the well-tempering parameters for each l we minimised the total CISD energy of the lithium atom with all electrons active.

Basis sets designed to reproduce the atomic energies may not be equally satisfactory in a molecular environment. This is especially true for weakly bound systems where the tails of the electronic density are important for the bonding phenomena. To assure that the basis sets developed here are truly universal we supplemented them with two sets of diffuse functions, see Table I. The exponents of these functions were varied freely to maximise the static dipole polarisability of the lithium atom evaluated at the coupled Hartree-Fock level of theory. The modified (augmented) basis sets are denoted da-wtcc-l where "da" stands for doubly augmented.

TABLE II. Total energy ($E_{\rm total}$) and the correlation energy ($E_{\rm corr}$) of the lithium atom calculated at the FCI level of theory by using the STOs basis sets da-wtcc-l. All values are given in the atomic units.

l	$E_{\rm corr}$	$E_{\rm total}$
2	−0.041 842	−7.474 511
3	−0.043 749	−7.476 454
4	−0.044 532	−7.477 239
5	−0.044 862	−7.477 569
6	−0.045 056	−7.477 763
∞	−0.045 386	−7.478 093
Ref. [83]	−0.045 353	−7.478 060

Finally, in this work we are concerned with calculation of the relativistic corrections which have somewhat specific basis set requirements. To eliminate possible sources of error we created a special sequence of basis sets denoted (da-)wtcc-l+s. These basis sets share the polarisation and/or augmented functions with the standard (da-)wtcc-l, but all s functions were replaced with a universal set of twelve $1s$ orbitals obtained by minimising the Hartree-Fock energy of the lithium atom. Detailed compositions of all basis sets used in this work (including values of the nonlinear parameters) are given in Supplemental Material [85].

As a benchmark of the newly developed basis sets we compared our atomic results with the reference values available in the literature. For the lithium atom very accurate value of the clamped-nucleus nonrelativistic energy is available [83] from the three-body Hylleraas calculations, $E_{\rm total} = 7.4780603239041\binom{+10}{-50}$. This value is virtually exact for the present purposes. For comparison, we calculated Hartree-Fock and FCI correlation energies in the da-wtcc-l basis sets, see Table II.

The Hartree-Fock energy converges at an exponential rate. Indeed, by comparing the results from the largest two basis set we see that the energy difference is less than 1μH. Therefore, we simply take the value from the largest basis set, $E_{\rm HF} = -7.432\ 707(1)$, and conservatively assume that the error is at most 1μH. Extrapolation of the HF energies by using the exponential formula barely changed the results. On the other hand, the correlation energy converges at a much slower rate and we apply the conventional two-point extrapolation [84]

$$E = a + \frac{b}{l^3} + \frac{c}{l^5}, \tag{3}$$

where the constants a, b, c are obtained by fitting. In Table II we present results obtained with the basis sets $l = 2-6$ and the values obtained by the extrapolation. Note that our final number for the total energy of the lithium atom differs by only about 34 μH ($\approx$7 cm^{-1}) from the aforementioned reference value.

TABLE III. Nonrelativistic contributions to the interaction energy of the lithium dimer (see the main text for explanation of the abbreviations) calculated with the da-wtcc-l basis sets. All values are given in wavenumbers, cm^{-1}.

l	$E_{\rm int}^{\rm HF}$	$E_{\rm int}^{\rm ccsd(t)}$	$\Delta E_{\rm int}^{\rm ccsdt}$	$\Delta E_{\rm int}^{\rm fci}$
		$R = 7.75$		
2	−359.46	276.40	1.45	0.15
3	−345.15	322.50	2.28	—
4	−344.14	328.30	2.29	—
5	−344.05	329.21	—	—
6	−344.10	329.51	—	—
∞	-344.05 ± 0.01	330.00 ± 0.25	2.30 ± 0.12	0.18 ± 0.05
		$R = 12.5$		
2	−9.64	73.79	0.22	0.05
3	−9.51	85.83	0.30	—
4	−9.46	87.05	0.30	—
5	−9.45	87.26	—	—
6	−9.44	87.74	—	—
∞	-9.42 ± 0.01	88.95 ± 0.61	0.30 ± 0.02	0.06 ± 0.02

B. Born-Oppenheimer potential

Lithium dimer is a two-centre six-electron molecule. For such system the FCI method, which gives the exact solution of the Schrödinger equation in the CBS limit, cannot be applied. Therefore, in the present work we rely on a composite method which is based mostly on the coupled cluster (CC) theory. The total interaction energy is divided into a set of well-defined components which are calculated separately assuming the additive nature of the corresponding physical effects. Our protocol for obtaining accurate Born-Oppenheimer interaction energies is as follows.

First, we evaluate the Born-Oppenheimer (BO) interaction energies by using the Hartree-Fock and CCSD(T) [86] methods (all electrons active). The values obtained are abbreviated shortly $E_{\rm int}^{\rm HF}$ and $E_{\rm int}^{\rm ccsd(t)}$, respectively. At these levels of theory the complete sequence of basis sets, $l = 2-6$, can be used. The Hartee-Fock and correlation contributions are extrapolated separately - the exponential formula is used for the HF component and the formula (3) is applied for the remainder. In Table III we present results of this procedure for two interatomic distances - 7.75 a.u. and 12.5 a.u. The former value is near the minimum of PEC whilst the latter lies close to the dissociation limit. To eliminate the basis set superposition error we apply the usual counterpoise correction, i.e. the energies of the monomers are calculated in the basis set of the dimer [87].

Interestingly, there is a small inconsistency in the Hartee-Fock values - the interaction energy calculated with the $l = 6$ basis set is by a tiny bit smaller than with $l = 5$. To overcome this problem we extrapolate

the HF limit from the $l = 3, 4, 5$ basis sets, omitting the $l = 6$ value. Due to comparatively fast convergence of the HF energies towards the CBS limit the error introduced by this approximation is minor for all interelectronic distances. More importantly, this artifact is absent in the correlated contribution and thus not of a major concern. In the estimation of the extrapolation errors we adopt a fairly conservative approach. Unless explicitly stated otherwise, we assume that the uncertainty is equal to a half of the difference between the extrapolated result and the corresponding value in the largest basis set.

To bring the accuracy down to the sub-wavenumber regime we need to consider some minor corrections beyond the CCSD(T) model. They naturally split into two contributions. The first is the full triples correction, being defined as a difference between the interaction energies obtained with the CCSDT and CCSD(T) methods, i.e. $\Delta E_{\rm int}^{\rm ccsdt} = E_{\rm int}^{\rm ccsdt} - E_{\rm int}^{\rm ccsd(t)}$. The second correction accounts for excitations higher than triple and is calculated as a difference between the FCI and CCSDT interaction energies, $\Delta E_{\rm int}^{\rm fci} = E_{\rm int}^{\rm fci} - E_{\rm int}^{\rm ccsdt}$. The post-CCSD(T) corrections are especially computationally intensive. In fact, we were able to calculate $\Delta E_{\rm int}^{\rm ccsdt}$ in basis sets only up to $l = 4$. Even more disappointingly, the FCI correction is feasible only in the smallest basis set considered here, $l = 2$. These restrictions eliminate the possibility of a reliable extrapolation.

To estimate the CBS limits of the post-CCSD(T) corrections we invoke a different strategy. Let us assume that the rate of convergence of the interaction energy with respect to the basis set size is the same at the CCSD(T) level and for the post-CCSD(T) corrections. Because a reliable limit of the CCSD(T) interaction energy is known, approximate CBS limits of the $\Delta E_{\rm int}^{\rm ccsdt}$ and $\Delta E_{\rm int}^{\rm fci}$ corrections can now be obtained by a simple scaling. The scaling parameter is chosen so that the interaction energy calculated with a given finite basis set at the CCSD(T) level matches the extrapolated value.

Clearly, the scaling procedure is not as reliable as extrapolation, the latter having firm theoretical underpinnings. We assume that this procedure gives an accuracy of 5% for $\Delta E_{\rm int}^{\rm ccsdt}$ and 25% for $\Delta E_{\rm int}^{\rm fci}$. The results of the scaling are given in Table III. The final theoretical error is computed by summing squares of the uncertainties in the individual components and taking the square root. For example, at the internuclear distance $R = 7.75$ this gives 332.48 ± 0.28 cm^{-1} for the total BO interaction energy.

C. Relativistic effects

For light systems, such as the lithium dimer, the leading-order relativistic corrections (quadratic in the fine structure constant, α) can be calculated perturbatively. Here we adopt the approach based on the one-electron part of the Breit-Pauli Hamiltonian [88]

TABLE IV. Relativistic corrections to the interaction of the lithium dimer energy calculated with the da-wtcc-l basis sets [see, Eqs. (4)-(6)]. The last column provides sums of the values from the preceding two. All values are given in wavenumbers, cm^{-1}.

l	$\langle P_4\rangle$	$\langle D_1\rangle$	total Cowan-Griffin
		$R = 7.75$	
2	−0.85	0.63	−0.22
3	−0.91	0.67	−0.24
4	−0.91	0.67	−0.24
5	−0.92	0.68	−0.24
		$R = 12.5$	
2	−0.11	0.08	−0.03
3	−0.13	0.09	−0.04
4	−0.13	0.09	−0.04
5	−0.14	0.10	−0.04

$$E^{(2)} = \langle P_4\rangle + \langle D_1\rangle, \tag{4}$$

$$\langle P_4\rangle = -\frac{\alpha^2}{8}\langle\sum_i \nabla_i^4\rangle, \tag{5}$$

$$\langle D_1\rangle = \frac{\pi}{2}\alpha^2 \sum_a Z_a \langle\sum_i \delta(\mathbf{r}_{ia})\rangle, \tag{6}$$

where i and a denote electrons and nuclei, respectively. The notation $\langle\hat{\mathcal{O}}\rangle$ stands for the expectation value of an operator $\hat{\mathcal{O}}$ on the nonrelativistic clamped-nuclei wavefunction. For brevity, the consecutive terms in the above equation are called the mass-velocity $\langle P_4\rangle$ and the one-electron Darwin $\langle D_1\rangle$ corrections. Some authors [89] use the name "Cowan-Griffin correction" for the sum of $\langle P_4\rangle$ and $\langle D_1\rangle$. For the fine structure constant we adopt the latest value recommended by CODATA, $\alpha^{-1} = 137.035\,999\,139$.

Note that in the above formulation we neglected the spin-spin and spin-orbit interactions. The former term is very small (≈ 0.01 cm^{-1} for all points of the potential energy curve) as confirmed by the recent work of Minaev [90], and vanishes quickly with the internuclear distance. The spin-orbit interaction is identically zero in the first-order perturbation theory since we are considering the molecular Σ state. The other two-electron (scalar) relativistic effects contribute less than ≈ 0.02 cm^{-1} at each point of the PEC and thus can be safely neglected at present.

The one-electron relativistic corrections were calculated analytically on the top of the CCSD(T) wavefunction. Contractions with the appropriate density matrices were accomplished by using a code written especially for this task. Because the CCSD(T) method performs very

well for the interaction energies, we neglect the higher-order mixed relativistic/correlation contributions and apply no post-CCSD(T) corrections. Exemplary results of the calculations are given in Table IV, where, for consistency, we consider the same two interatomic distances as in the preceding section. To speed up the calculations, we evaluated the one-electron relativistic corrections in the basis sets up to $l = 5$ only.

From Table IV one can see that the mass-velocity and one-electron Darwin corrections converge very quickly with respect to the basis set size. The results in the two largest basis sets are barely distinguishable. Therefore, it is not necessary to extrapolate the values of $\langle P_4 \rangle$ and $\langle D_1 \rangle$. The final result is simply the value obtained with the largest basis set and the error is estimated to be less than 5% of the absolute value.

D. Other corrections

Since the goal of the present paper is to reach the spectroscopic accuracy we have to include some further corrections to the potential energy curve originating from the QED and adiabatic effects. Starting with the former, the most convenient framework to describe the QED effects in light systems is the so-called non-relativistic QED (NRQED) theory [91, 92]. In the NRQED the energy of the system is expanded in powers of the fine-structure constant. The quadratic terms correspond to the aforementioned Breit-Pauli Hamiltonian and the α^3 and $\alpha^3 \ln \alpha$ corrections are the leading-order (pure) QED effects, $E^{(3)}$. Explicit expressions for the latter are known [93, 94], but their computation for many-electron systems is still a considerable challenge. In the present work we adopt the following approximation to the α^3 and $\alpha^3 \ln \alpha$ corrections

$$E^{(3)} \approx \frac{8\alpha}{3\pi} \left(\frac{19}{30} - 2 \ln \alpha - \ln k_0^{\mathrm{Li}} \right) \langle D_1 \rangle, \qquad (7)$$

where $\ln k_0$ is the Bethe logarithm [88, 95] and $\langle D_1 \rangle$ is the same as in Eq. (6). This is essentially the dominant one-electron component of the complete α^3 QED correction (the one-electron Lamb shift). For the Bethe logarithm we adopt the atomic value, $\ln k_0^{\mathrm{Li}} = 5.178\,17(3)$ [96]. This is a reasonable approximation because this quantity is usually weakly dependent on the molecular geometry [97, 98]. We assume that the approximations introduced in (7) are accurate to within 50% of the total value.

Finally, let us consider the finite nuclear mass effects. The leading-order correction to the PEC due to the nuclear motion is the so-called diagonal Born-Oppenheimer correction (or the adiabatic correction for short). It is given by the formula [99, 100]

$$E_{\mathrm{DBOC}} = \frac{1}{2} \sum_A \frac{1}{M_A} \langle \nabla_A \Psi_0 | \nabla_A \Psi_0 \rangle, \qquad (8)$$

where A runs over all nuclei of the system and M_A denote the nuclear masses. Unfortunately, calculation of the DBOC with the basis set of STOs is not developed yet and we must resort to the GTOs in the present paper. We have used the all-electron CCSD method to calculate the adiabatic correction [101] with the augmented quadruple-zeta basis set developed by Prascher et al. [102] The post-CCSD corrections and basis set incompleteness errors are neglected in this case. We assume that this introduces an error of at most 25%.

E. Computational details

For the record, in this section we would like to provide some additional technical details concerning the electronic structure calculations described above. The basis set optimisations were carried out by using a program written especially for this purpose. It is interfaced with the Gamess package [103, 104] which carries out the necessary CISD calculations. To optimise the well-tempering parameters we employed the pseudo Newton-Rhapson method with the BFGS update of the approximate Hessian matrix [105] and numerically evaluated gradient (two-point finite difference). The optimisations were stopped when the energy difference between two consecutive cycles fell below 10 nH.

All subsequent electronic structure calculations were carried out with help of the AcesII program package [106]. The only exception is the FCI method where the Gamess package was used and calculation of the adiabatic correction where we employed the CFour program [107]. In all coupled cluster computations we employed the restricted open-shell (RO) reference wavefunction. Inclusion of the relativistic corrections requires expectation values of several operators specified in the preceding sections. Matrix elements of these operators were calculated directly in the STOs basis sets. Coupled cluster density matrices were extracted from the AcesII package by proper manipulation of the CC gradients code logic.

To evaluate the complete potential energy curve we repeated the procedures described in the preceding sections on a grid of internuclear distances. For the non-relativistic calculations we used the following grid: from $R = 5.5$ to $R = 9.0$ the step is $R = 0.25$; from $R = 9.0$ to $R = 14.0$ it is $R = 0.5$; from $R = 14.0$ to $R = 25.0$ it is $R = 1.0$, and finally above $R = 25.0$ the step is $R = 2.5$ up to $R = 40.0$ (all values are given in multiples of the Bohr radius). Additionally, we evaluated a single point at $R = 7.882$ which is close to the actual minimum of the potential energy curve. This gives a grand total of 43 points spaced from $R = 5.5$ to $R = 40.0$. For the relativistic corrections the grid was slightly smaller ending at $R = 30.0$. This mostly due to large cancellations occurring at large R making the calculated values less reliable.

TABLE V. Optimised parameters of the fit (9) for the Born-Oppenheimer potential [$V^{\rm BO}(R)$] and for the adiabatic correction [$V^{\rm ad}(R)$] (without dividing by the mass term). All values are given in the atomic units. The symbol $X[\pm n]$ stands for $X \cdot 10^{\pm n}$. Not all digits reported are significant.

parameter	$V^{\rm BO}(R)$	$V^{\rm ad}(R)$
α_1	+1.27 983[+00]	+1.87 631[+00]
α_2	+2.29 122[−01]	+3.24 019[−01]
η	+1.02 337[+00]	+5.84 617[−01]
c_{01}	+1.28 843[+02]	−8.45 797[+00]
c_{11}	−9.02 013[+01]	+4.52 239[+00]
c_{21}	+2.67 910[+01]	−8.14 315[−01]
c_{31}	−3.42 393[+00]	+5.01 342[−02]
c_{41}	+2.07 665[−01]	—[b]
c_{02}	+2.11 421[−03]	+1.95 248[−06]
c_{12}	−2.40 579[−04]	−5.40 041[−08]
c_{22}	+1.05 528[−05]	−1.43 211[−08]
c_{32}	−2.07 608[−07]	+4.64 261[−10]
c_{42}	+1.54 659[−09]	—[b]
C_6	+1.39 339[+03][a]	+1.47 084[+00]
C_8	+8.34 258[+04][a]	−1.18 756[+03]
C_{10}	+7.37 210[+06][a]	+4.05 449[+05]
C_{12}	+9.03 000[+08][a]	—[b]
C_{14}	+1.48 000[+11][a]	—[b]
C_{16}	+3.09 000[+13][a]	—[b]

[a]taken from Refs. [111] and [112] [b]not included in the fit

TABLE VI. Optimised parameters of the fit (9) for the one-electron relativistic corrections - mass-velocity [$V^{\rm P4}(R)$] and one-electron Darwin [$V^{\rm D1}(R)$], see Eqs. (5) and (6), respectively, for the definitions. All values are given in the atomic units. The symbol $X[\pm n]$ stands for $X \cdot 10^{\pm n}$.

parameter	$V^{\rm P4}(R)$	$V^{\rm D1}(R)$
α_1	+1.3284[+00]	+1.3624[+00]
α_2	+4.9227[−01]	+5.2275[−01]
η	+3.2767[−01]	+3.7855[−01]
c_{01}	−1.2702[−01]	+1.4557[−01]
c_{11}	+8.8288[−02]	−9.7541[−02]
c_{21}	−2.1025[−02]	+2.2358[−02]
c_{31}	+1.9023[−03]	−1.9527[−03]
c_{02}	−1.4425[−03]	+1.3737[−03]
c_{12}	+2.6974[−04]	−2.5064[−04]
c_{22}	−1.4610[−05]	+1.3126[−05]
c_{32}	+2.8967[−07]	−2.5278[−07]
C_6	−2.2228[+00]	+1.5773[+00]
C_8	−8.9706[+01]	+7.3228[+01]
C_{10}	−1.9637[+04]	+1.0532[+05]

III. ANALYTIC FITS OF THE POTENTIALS

A. General method

In order to generate results directly comparable with the experimental values, the raw *ab initio* data points must be fitted with a suitable functional form to give a smooth function of the internuclear distance, R. For all contributions to the interaction energy described in the previous sections we adopt the following generic formula

$$V(R) = \sum_{k=1}^{N_e} e^{-\alpha_k R} \sum_{n=0}^{N_p} c_{nk} R^n - \sum_{n=3}^{N_a} \frac{C_{2n}}{R^{2n}} f_{2n}(\eta R), \quad (9)$$

where N_e, N_p and N_a control the expansion length, α_k and η are (nonlinear) parameters of the fit, c_{nk} are linear parameters, and $f_{2n}(\eta R)$ is the Tang-Toennies damping function [108]

$$f_{2n}(x) = 1 - e^{-x} \sum_{k=0}^{2n} \frac{x^k}{k!}. \quad (10)$$

The asymptotic coefficients, C_{2n}, in Eq. (9) are either taken from more accurate theoretical calculations or fitted (discussed further). Note that we found it unnecessary to include the repulsive Coulomb wall (the unified atoms limit, Z^2/R) in the potential formula (9) .

The nonlinear and linear parameters in Eq. (9) are chosen to minimise weighted error of the fit. At each point of the grid we are given the values of the potential, $V_k^{\rm comp}$, and the corresponding errors, $\delta V_k^{\rm comp}$. The target function Δ for the optimisation is chosen as

$$\Delta^2 = \frac{1}{N_g} \sum_{k=1}^{N_g} \left[\frac{V_k^{\rm comp} - V(R_k)}{\delta V_k^{\rm comp}} \right]^2, \quad (11)$$

where $V(R_k)$ is the value of the fitting function evaluated at a given grid point. We optimise the nonlinear parameters by using the Powell procedure [109]. The optimisation is stopped when the target function varies by less than 10^{-5} cm^{-1} between several consecutive iterations. The raw *ab initio* data ($V_k^{\rm comp}$, $\delta V_k^{\rm comp}$) for all components of the PEC are given in the Supplemental Material [85]. A simple MATHEMATICA program [110] implementing all the fits discussed here can be obtained from the authors upon request.

B. Nonrelativistic potentials

An important issue in the generation of the analytic potentials is to assure that the long-range tail of PEC is correct. Therefore, we prefer to use the asymptotic constants calculated with more accurate theoretical methods (whenever available) rather to rely solely on fitting to match the data points. Fortunately, reliable values of

the first three nonrelativistic asymptotic constants (C_6, C_8, C_{10}) were given by Yan et al. [111] These values were obtained from variational wave functions in Hylleraas basis sets and are all accurate to better than one part per thousand. For the higher asymptotic constants (C_{2n} with $n > 5$) the data in the literature are not as abundant. Remarkably, Patil et al. [112] report values of the asymptotic constants up to $n = 12$. Their values are progressively less reliable with increasing n. For example, we find that the error in C_6 is only about 0.3% compared with the work of Yan et al. [111] but rises to almost 2% for C_{10}. Therefore, we adopt the values of C_{12}, C_{14} and C_{16} from Ref. [112] and neglect the higher-order inverse powers of R in Eq. (9). We checked that the inclusion of terms beyond C_{16} changes the results only marginally. The same is true for the asymptotic terms such as C_{11}/R^{11} (resulting from higher-order perturbation theory) which can be safely neglected at this point.

Concerning the adiabatic correction, the corresponding asymptotic constants are not available for lithium. Despite explicit expressions for these coefficients are available in the literature [113], their calculation is complicated and has been achieved only for one- and two-electron systems thus far. Therefore, we have no other option but to obtain the asymptotic constants $C_{2n}^{\rm ad}$ by fitting. We find that inclusion of the first three coefficients is sufficient to provide a reasonable accuracy.

Overall, the fitting function (9) with $N_e = 2$, $N_p = 3$ or 4, and $N_a \leq 8$ provides a satisfactory representation of the raw *ab initio* data, both for the Born-Oppenheimer results [$V^{\rm BO}(R)$, $N_p = 4$, $N_a = 8$] and for the adiabatic correction [$V^{\rm ad}(R)$, $N_p = 3$, $N_a = 5$]. Both fits contain 10 linear and 3 nonlinear parameters which is a modest amount compared to about 40 points of the raw *ab initio* data. The fitting errors are by an order of magnitude smaller than the estimated uncertainty of the corresponding theoretical calculations. Only one or two points are exceptional in this respect, but the error is still well within the acceptable range. Optimised parameters of the Born-Oppenheimer and adiabatic potentials are given in Table V. Note that the adiabatic correction fitting error is larger than for the BO potential [cf. Table VII] but this mostly due to increased relative errors $\delta V_k^{\rm comp}$ and smaller number of fitting parameters.

C. Relativistic effects

Analytic potentials corresponding to the one-electron relativistic effects were obtained in a similar fashion as for the adiabatic correction. The mass-velocity [Eq. (5)] and one-electron Darwin [Eq. (6)] terms were separately represented in the form given by Eq. (9) with $N_e = 2$, $N_p = 3$, $N_a = 5$. The optimised parameters are given in Table VI. For convenience, in both cases we have included the factor of α^2 into the coefficients.

Note that the last asymptotic constant (C_{10}) in both fits optimised to a surprisingly large value. We believe that this result should be treated cautiously. Whilst the first two asymptotic coefficients are reasonably stable with respect to various modifications of the fitting formula, the last one depends significantly on the adopted parametrisation. In order to stabilise this quantity one would need to include more asymptotic terms, but because of the risk of over-parametrisation, we decided not to do it. Therefore, the obtained values of C_{10} should not be used as a reference for other methods. The same conclusion is probably valid for the fit of the adiabatic correction described in the previous section.

TABLE VII. Root mean square deviations (in $\rm cm^{-1}$) and maximum absolute deviations (percentage-wise) of the fitted values from the raw data points. The symbol $X[\pm n]$ stands for $X \cdot 10^{\pm n}$.

	rms error	max error (%)
$V^{\rm BO}(R)$	1.8[−01]	3.0[−01]
$V^{\rm D1}(R)$	3.6[−05]	6.7[−02]
$V^{\rm P4}(R)$	8.1[−05]	6.1[−02]
$V^{\rm ad}(R)$	6.0[−03]	4.7[+00]

The accuracies of the fitting functions for are summarised in Table VII. More detailed data are given in Supplemental Material [85]. This includes explicit listing of the raw *ab initio* values at each point and the corresponding errors.

IV. SPECTROSCOPIC DATA

In order to generate the spectroscopic data we add up all components of the PEC described above (BO, adiabatic, relativistic and QED). The final PEC is illustrated in Fig. IV. Based on the complete curve we calculate the relevant molecular parameters. The total binding energy (i.e. the well depth, D_e) and the equilibrium internuclear distance (R_e) are obtained by finding the minimum of the fitted PEC. The harmonic vibrational frequency is defined as

$$\omega_e^2 = \frac{1}{\mu}\left(\frac{\partial^2 V}{\partial R^2}\right)\Big|_{R_e}, \tag{12}$$

in the atomic units, where μ is the reduced mass of an isotopomer. We consider two stable isotopes of lithium (^{6}Li and ^{7}Li) with the atomic masses equal to

$$m(^6\mathrm{Li}) = 6.015\ 123\ \mathrm{u}, \tag{13}$$

$$m(^7\mathrm{Li}) = 7.016\ 005\ \mathrm{u}, \tag{14}$$

according to the recent compilation [114]. Conversion factor from the unified atomic mass unit (u) to the atomic units is approximately 1822.888 [115].

In order to find the rovibrational wavefunctions ($\Psi_{\nu J}$) and energies ($E_{\nu J}$) we solve the nuclear (radial)

TABLE VIII. Molecular parameters of the $a^3\Sigma_u^+$ state of $^{6,6}Li_2$ and $^{7,7}Li_2$. See the main text for precise definitions of the listed quantities. All values are given in wavenumbers, cm^{-1}, apart from R_e which are given in Ångströms, Å.

	D_e	R_e	D_0	ω_e
	$^{6,6}Li_2$			
this work	333.68(30)	4.1688	299.13	71.05
Ref. [54]	333.778(8)	4.170038(30)	—	70.65[a]
	$^{7,7}Li_2$			
this work	333.69(30)	4.1687	301.61	65.78
Ref. [54]	333.758(7)	4.17005(3)	—	65.42[a]
Ref. [24]	333.69(10)	4.173	301.829(15)	—

[a]not reported originally in Ref. [54]; extracted by taking the second derivative of the final potential

Schrödinger equation

$$\left[-\frac{1}{2\mu}\frac{d^2}{dR^2} + D_e + V(R) + \frac{J(J+1)}{2\mu R^2} - E_{\nu J}\right]\Psi_{\nu J}(R) = 0, \tag{15}$$

where J is the rotational quantum number. No that we have added the well-depth (D_e) to the left-hand-side of Eq. (15). This makes all $E_{\nu J}$ positive by convention and their values grow with the increasing values of ν and J. Further in the paper we are mostly concerned with the lowest rotational state ($J = 0$) and thus adopt the notation $E_\nu := E_{\nu 0}$. Finally, the dissociation energy is defined as a sum of the interaction energy and the zero-point vibrational energy, $D_0 = D_e + E_{\nu=0}$.

In Table VIII we report the calculated *ab initio* values of the molecular parameters (D_e, R_e, D_0, ω_e) for both isotopomers of the lithium dimer. The error of D_e was estimated by interpolating the theoretical errors at several neighbouring grid points. Let us compare our results with the most recent experimental values of Linton et al. [24] and with a very reliable 17-parameter Morse/long-range potential of Dattani and Le Roy [54]. The agreement with these values is remarkably good. For example, our D_e for the isotopomer $^{7,7}Li_2$ differs from the results of Refs. [24] and [54] by only 0.01 and 0.07 cm^{-1}, respectively, while our estimated error is about 0.3 cm^{-1} at the bottom of the well. The same conclusion is valid for the dissociation energy, D_0. This suggest that our error estimations are indeed quite conservative, at least in the regions close to the minimum of the potential. A similarly good agreement is found for the remaining molecular parameters.

The radial nuclear Schrödinger equation (15) was solved with help of the discrete variable representation (DVR) method [116]. The obtained vibrational energy levels ($J = 0$) are listed in Table IX and compared with the experimental values of Linton et al. [24]. Additionally, we calculate the classical turning points (R^ν) defined as solutions of the following implicit equations

$$D_e + V(R^\nu) = E_\nu. \tag{16}$$

For each ν we have two solutions of Eq. (16), denoted $R^\nu_{\rm min}$ and $R^\nu_{\rm max}$, and both of them are listed in Table IX.

One can see an excellent agreement between the theoretical and experimental vibrational energy levels, Table IX. The maximum absolute deviation is found for $\nu = 7$ and amounts to about 0.4 cm^{-1}. On average, the deviation is of the order of 0.3 cm^{-1}. Let us point out that resolution of the spectroscopic data of Linton et al. is about 0.1 cm^{-1}, so that the actual error of our calculations can be even smaller. Moreover, our *ab initio* values are more accurate than reported recently by Lau et al. [55] based on a semi-empirical model potential. Their data exhibits the maximum E_ν deviation of about 1.5 cm^{-1} if they use the accurate ω_e in the potential. By relaxing the value of ω_e by about 1% the accuracy improves to about 0.5 cm^{-1} on the average, but this may be due to a fruitful cancellation of errors. In fact, our results support the semiempirical value of ω_e. Let us also point out that our potential reproduces the binding energy of the last vibrational level with surprising accuracy. While the experimentally derived value is 12.47 ± 0.04 GHz [49] the PEC developed in this work gives 10.5 GHz.

Let us now turn our attention to theoretical description of the Li−Li scattering process. The main goal is to evaluate the s-wave scattering length (a) for two lithium atoms in the ground state from the first-principles PEC developed in this work. This can be accomplished by

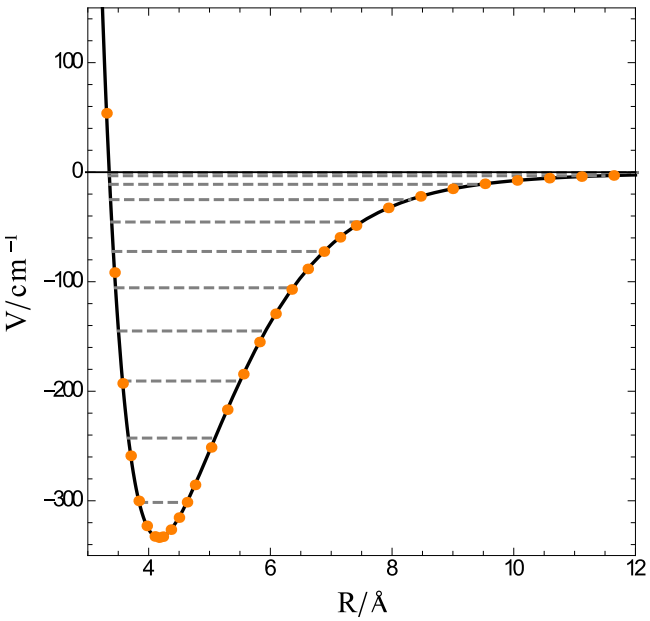

FIG. 1. Complete potential energy curve for the for the $a^3\Sigma_u^+$ state of $^{7,7}Li_2$ (solid black line); orange dots are the actual *ab initio* data points. The horizontal dashed lines are energies of the $J = 0$ vibrational levels. The horizontal black solid line denotes the onset of continuum.

TABLE IX. Vibrational energy levels ($J = 0$) for the $a^3\Sigma_u^+$ state of $^{7,7}Li_2$. The vibrational energies (E_ν) are given in wavenumbers, cm^{-1}, and the classical turning points (R^ν_{min}, R^ν_{max}) in Ångströms, Å. The minimum of PEC corresponds to the zero energy. The last two rows are the maximum and root-mean-square errors with respect to the experimental data [24].

	this work			Ref. [24]		
ν	E_ν	R^ν_{min}	R^ν_{max}	E_ν	R^ν_{min}	R^ν_{max}
0	32.06	3.844	4.627	31.857	3.846	4.630
1	90.83	3.668	5.090	90.453	3.668	5.092
2	142.94	3.570	5.502	142.523	3.571	5.503
3	188.65	3.504	5.920	188.240	3.505	5.922
4	228.07	3.455	6.371	227.679	3.458	6.373
5	261.24	3.419	6.882	260.837	3.422	6.885
6	288.11	3.392	7.496	287.665	3.395	7.501
7	308.55	3.373	8.293	308.098	3.377	8.297
8	322.55	3.361	9.453	322.155	3.365	9.441
9	330.39	3.354	11.476	330.170	3.358	11.392
10	333.32	3.352	16.478	333.269	3.356	16.052
δ_{max}	0.45	0.004	0.424	—	—	—
δ_{rms}	0.34	0.003	0.130	—	—	—

solving the radial Schrödinger equation (15) with $J = 0$ at zero energy [117]. It is well known that for large R the solutions $\Psi_{E=0}(R)$ behave asymptotically as a linear function [118, 119]

$$\Psi_{E=0}(R) \to C\,(R - a) + \ldots, \tag{17}$$

where a is the desired scattering length. Very sophisticated methods for numerical calculation of a were presented [120–123], but our case is not particularly technically challenging and we adopt the following simplistic procedure. First, we propagate the radial Schrödinger equation at zero energy up to very large R ($\approx 10^5$). The initial conditions are $\Psi_{E=0}(R_0) = 0$, where R_0 is deep within the repulsive wall, and an arbitrary value of the derivative at R_0. Next, we continue the asymptotic straight line (17) to the point where it crosses the r-axis. By the virtue of Eq. (17) this point corresponds to the value of a.

positive behave

The s-wave scattering length for the $^{7,7}Li_2$ isotopomer calculated from the PEC developed in this work is -9.2 a.u. This is by a factor of three too small compared with the experimental result of Abraham et al. [49] who report -27.3 ± 0.8 a.u. Despite this deviation is large we note that the sign of the scattering length calculated by us is correct. This is sufficient to predict the stability of the corresponding Bose-Einstein condensate [124, 125]. Moreover, the rough magnitude of the scattering length is also correct which makes it useful for other predictions [126, 127]. To predict a with the accuracy of a few percents the errors in PEC must be reduced probably by an order of magnitude. We believe that this is possible in a foreseeable future.

V. CONCLUSIONS

In this paper we have developed a new *ab initio* potential energy curve for the $a^3\Sigma_u^+$ state of lithium dimer. To bring down the accuracy to the sub-wavenumber regime we have employed state-of-the-art techniques of the electronic structure theory. In particular, large (double to sextuple zeta) one-electron basis sets composed of Slater-type orbitals have been developed specifically for the present purposes. The Born-Oppenheimer potential has been calculated by using a composite scheme utilising high-order coupled cluster and full CI methods. Moreover, we have included several minor corrections beyond the Born-Oppenheimer picture - the adiabatic, relativistic, and QED effects.

The computed *ab initio* data points have been fitted with theoretically motivated analytic functions. When available, we employed van der Waals asymptotic constants C_n obtained from the most accurate theoretical methods. By solving the nuclear Schrödinger equation we have obtained the molecular parameters (D_e, D_0, ω_e etc.) for this system, as well as the corresponding vibrational energy levels, which are directly comparable with the experimental data. For example, the bond dissociation energy determined by us ($D_0 = 301.61$ cm^{-1}) differs by only about 0.2 cm^{-1} from the empirical values reported by Linton et al. [24] We have also reproduced all eleven bound vibrational levels with accuracy of $0.2 - 0.4\,cm^{-1}$. In particular, the position of the last vibrational level has been predicted to within 2 GHz or 15% of the experimental value. Crucially, all these results have been obtained without prior adjustment to match the empirical values.

The data presented in this paper are probably the most accurate *ab initio* results available for this system in the literature thus far. Moreover, this paper constitutes a proof that Slater-type orbitals can now be used routinely in calculations for the diatomic systems with large basis sets (up to several hundred functions) and are capable of providing spectroscopically accurate results.

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TABLE I. Born-Oppenheimer raw data used for fitting. The columns denote (in the consecutive order): internuclear distances, calculated (total) Born-Oppenheimer interaction energies, estimated theoretical uncertainties, deviations of the fit from the calculated values, deviations of the fit divided by the theoretical uncertainties.

R_k/a.u.	$V_k^{\rm comp}/{\rm cm}^{-1}$	$\delta V_k^{\rm comp}/{\rm cm}^{-1}$	$\left\|V_k^{\rm comp} - V^{\rm BO}(R_k)\right\|/{\rm cm}^{-1}$	$\left\|V_k^{\rm comp} - V^{\rm BO}(R_k)\right\|/\ \delta V_k^{\rm comp}$
5.50	941.20	0.90	0.49	0.55
5.75	547.74	0.85	0.64	0.76
6.00	260.27	0.83	0.10	0.13
6.25	53.80	0.75	0.055	0.074
6.50	−91.62	0.68	0.27	0.40
6.75	−192.81	0.60	0.59	0.98
7.00	−258.92	0.53	0.24	0.46
7.25	−300.12	0.44	0.076	0.17
7.50	−322.92	0.39	0.12	0.30
7.75	−332.57	0.32	0.16	0.50
7.88	−333.65	0.28	0.15	0.54
8.00	−332.77	0.25	0.13	0.52
8.25	−326.34	0.19	0.077	0.41
8.50	−315.36	0.13	0.023	0.17
8.75	−301.30	0.10	0.037	0.37
9.00	−285.50	0.078	0.071	0.91
9.50	−251.28	0.066	0.17	2.5
10.0	−216.82	0.062	0.14	2.3
10.5	−184.38	0.066	0.061	0.92
11.0	−155.05	0.074	0.026	0.35
11.5	−129.28	0.085	0.077	0.91
12.0	−107.08	0.095	0.087	0.92
12.5	−88.32	0.11	0.017	0.15
13.0	−72.49	0.083	0.067	0.81
13.5	−59.46	0.090	0.0025	0.027
14.0	−48.73	0.088	0.047	0.53
15.0	−32.80	0.077	0.11	1.5
16.0	−22.09	0.057	0.045	0.79
17.0	−15.18	0.036	0.014	0.39
18.0	−10.59	0.022	0.0091	0.40
19.0	−7.535	0.014	0.0025	0.17
20.0	−5.451	0.0091	0.0025	0.28
21.0	−4.011	0.0060	0.0016	0.26
22.0	−2.997	0.0041	0.00067	0.16
23.0	−2.271	0.0029	0.00030	0.10
24.0	−1.743	0.0021	0.00028	0.13
25.0	−1.354	0.0016	0.00040	0.26
27.5	−0.752	0.00078	0.00018	0.23
30.0	−0.441	0.00043	0.000042	0.097
32.5	−0.271	0.00026	0.000068	0.27
35.0	−0.172	0.00016	0.000000	0.00039
37.5	−0.113	0.00010	0.000026	0.26
40.0	−0.070	0.000070	0.000008	0.11

TABLE II. Relativistic corrections raw data used for fitting. The columns denote (in the consecutive order): internuclear distances, calculated (total) Born-Oppenheimer interaction energies, estimated theoretical uncertainties in the values from the previous column, deviation of the fit at the given point, deviation of the fit at the given point divided by the theoretical uncertainty. The meaning of the remaining symbols is the same as in the main text.

R_k/a.u.	$V_k^{\rm comp}/{\rm cm}^{-1}$		$\delta V_k^{\rm comp}/{\rm cm}^{-1}$		$10^5\left\lvert V_k^{\rm comp}-V^{\rm BO}(R_k)\right\rvert/{\rm cm}^{-1}$		$10^3\left\lvert V_k^{\rm comp}-V^{\rm BO}(R_k)\right\rvert/\,\delta V_k^{\rm comp}$	
	$\langle P_4\rangle$	$\langle D_1\rangle$	$\langle P_4\rangle$	$\langle D_1\rangle$	$\langle P_4\rangle$	$\langle D_1\rangle$	$\langle P_4\rangle$	$\langle D_1\rangle$
5.50	0.641	−0.562	0.032	0.028	2.4	0.16	0.75	0.058
5.75	0.896	−0.726	0.045	0.036	11.6	1.4	2.6	0.39
6.00	1.06	−0.826	0.053	0.041	3.1	7.4	0.58	1.8
6.25	1.14	−0.875	0.057	0.044	15.2	0.27	2.7	0.061
6.50	1.17	−0.886	0.059	0.044	22.5	9.9	3.8	2.2
7.00	1.12	−0.832	0.056	0.042	0.31	7.2	0.055	1.7
7.25	1.06	−0.784	0.053	0.039	12.7	0.38	2.4	0.097
7.50	0.990	−0.728	0.049	0.036	18.6	6.1	3.8	1.7
7.75	0.913	−0.670	0.046	0.033	16.6	8.1	3.6	2.4
8.00	0.836	−0.611	0.042	0.031	9.3	6.6	2.2	2.2
8.25	0.760	−0.554	0.038	0.028	0.037	2.9	0.0098	1.05
8.50	0.688	−0.501	0.034	0.025	8.1	1.2	2.4	0.49
8.75	0.621	−0.451	0.031	0.023	13.2	4.5	4.3	2.0
9.00	0.559	−0.406	0.028	0.020	14.7	6.3	5.3	3.1
9.50	0.453	−0.328	0.023	0.016	9.3	5.4	4.1	3.3
10.0	0.367	−0.265	0.018	0.013	0.31	1.2	0.17	0.92
10.5	0.298	−0.215	0.015	0.011	7.0	2.3	4.7	2.2
11.0	0.243	−0.175	0.012	0.0088	8.4	3.7	6.9	4.2
11.5	0.199	−0.143	0.0099	0.0072	5.7	2.8	5.7	3.9
12.0	0.163	−0.117	0.0082	0.0059	1.6	1.1	2.0	1.8
12.5	0.134	−0.0965	0.0067	0.0048	1.8	0.60	2.7	1.3
13.0	0.111	−0.0794	0.0055	0.0040	3.5	1.5	6.3	3.8
13.5	0.0914	−0.0654	0.0046	0.0033	3.4	1.6	7.5	5.0
14.0	0.0755	−0.0539	0.0038	0.0027	2.2	1.1	5.8	4.0
14.5	0.0625	−0.0445	0.0031	0.0022	0.57	0.29	1.8	1.3
15.0	0.0517	−0.0368	0.0026	0.0018	0.90	0.40	3.5	2.2
16.0	0.0356	−0.0252	0.0018	0.0013	2.0	0.97	11.1	7.7
17.0	0.0246	−0.0175	0.0012	0.00087	1.2	0.57	9.4	6.5
18.0	0.0172	−0.0122	0.00086	0.00061	0.0064	0.035	0.075	0.58
19.0	0.0122	−0.00868	0.00061	0.00043	0.55	0.28	9.0	6.4
20.0	0.00882	−0.00627	0.00044	0.00031	0.42	0.21	9.5	6.8
21.0	0.00647	−0.00460	0.00032	0.00023	0.13	0.076	3.9	3.3
22.0	0.00482	−0.00343	0.00024	0.00017	0.095	0.066	3.9	3.9
23.0	0.00365	−0.00260	0.00018	0.00013	0.14	0.080	7.7	6.1
24.0	0.00280	−0.00199	0.00014	0.00010	0.010	0.052	7.1	5.2
25.0	0.00217	−0.00155	0.00011	0.000077	0.011	0.0049	1.0	0.63
27.5	0.00121	−0.000861	0.000060	0.000043	0.073	0.058	12.1	13.4
30.0	0.000709	−0.000505	0.000035	0.000025	0.020	0.018	5.8	6.9

TABLE III. Adiabatic correction raw data used for fitting (without the mass term). The columns denote (in the consecutive order): internuclear distances, calculated contribution of the term $\sum_A \langle \nabla_A \Psi_0 | \nabla_A \Psi_0 \rangle$ to the interaction energy, estimated theoretical uncertainties, deviations of the fit from the calculated values, deviations of the fit divided by the theoretical uncertainties. To get the actual contribution to the interaction energy the values in the second column must be divided by the respective isotope mass.

R_k/a.u.	$V_k^{\mathrm{comp}}/\mathrm{cm}^{-1}$	$\delta V_k^{\mathrm{comp}}/\mathrm{cm}^{-1}$	$\left\lvert V_k^{\mathrm{comp}} - V^{\mathrm{BO}}(R_k) \right\rvert/\mathrm{cm}^{-1}$	$\left\lvert V_k^{\mathrm{comp}} - V^{\mathrm{BO}}(R_k) \right\rvert/\ \delta V_k^{\mathrm{comp}}$
5.50	2.977	0.74	0.0035	0.0048
5.75	1.874	0.47	0.0030	0.0065
6.00	1.028	0.26	0.0011	0.0042
6.25	0.4456	0.11	0.0033	0.030
6.50	0.04866	0.012	0.000074	0.0061
6.75	−0.2182	0.055	0.0016	0.029
7.00	−0.3979	0.099	0.00047	0.0047
7.25	−0.5008	0.13	0.023	0.19
7.50	−0.6283	0.16	0.018	0.11
7.75	−0.6803	0.17	0.014	0.083
8.00	−0.7052	0.18	0.0070	0.040
8.25	−0.7157	0.18	0.0049	0.028
8.50	−0.7096	0.18	0.0018	0.010
8.75	−0.6909	0.17	0.0014	0.0082
9.00	−0.6614	0.17	0.0063	0.038
9.50	−0.5913	0.15	0.0092	0.062
10.0	−0.5162	0.13	0.0067	0.052
10.5	−0.4422	0.11	0.0032	0.029
11.0	−0.3737	0.093	0.00032	0.0034
11.5	−0.3127	0.078	0.0015	0.019
12.0	−0.2601	0.065	0.0025	0.038
12.5	−0.2148	0.054	0.0021	0.040
13.0	−0.1771	0.044	0.0017	0.038
13.5	−0.1458	0.036	0.0011	0.030
14.0	−0.1201	0.030	0.00054	0.018
14.5	−0.09901	0.025	0.000038	0.0015
15.0	−0.08177	0.020	0.00035	0.017
16.0	−0.05651	0.014	0.00049	0.035
17.0	−0.03973	0.0099	0.00034	0.034
18.0	−0.02833	0.0071	0.00021	0.029
19.0	−0.02063	0.0052	0.000017	0.0033
20.0	−0.01494	0.0037	0.00017	0.045
21.0	−0.01124	0.0028	0.000020	0.0071
22.0	−0.008469	0.0021	0.000019	0.0089
23.0	−0.006621	0.0017	0.00017	0.10
24.0	−0.005081	0.0013	0.000097	0.076
25.0	−0.003850	0.00096	0.000051	0.053
27.5	−0.002156	0.00054	0.000070	0.13
30.0	−0.001386	0.00035	0.000026	0.074

Paper VII

"Ab initio interaction energy curve for the ground state of beryllium dimer"

Michał Lesiuk, Michał Przybytek, Justyna Balcerzak, Monika Musiał, and Robert Moszyński

preprint

Commentary

The present work is a detailed first-principles theoretical study of the ground state of the beryllium dimer. An accurate *ab initio* potential energy curve for this system is calculated with a composite scheme involving several quantum-chemical methods and large basis sets composed of Slater-type orbitals. The dominant (four-electron) valence contribution to the interaction energy is calculated at the FCI level theory. The remaining inner-shell effects are treated with high-level coupled cluster methods such as CCSD(T) or CCSDT(Q).

To further increase the accuracy of our theoretical predictions we have perturbatively calculated corrections due to some small physical effects. This includes the relativistic corrections (full Breit-Pauli Hamiltonian) and the leading-order quantum electrodynamics (QED) corrections. This is also probably the first work in the literature where the complete α^3 QED correction is evaluated for a many-electron molecular system (approximating only the so-called Bethe logarithm). Relative importance of various QED corrections is discussed. The finite nuclear mass effects (the non-Born-Oppenheimer effects) are found to be negligible at present.

Spectroscopic parameters generated by using the PEC developed in this work show a remarkably good agreement with the best empirical data. This is true for the well-depth (calculated $D_e = 933.3 \pm 2.5\text{cm}^{-1}$ vs. empirical $D_e = 934.8 \pm 0.3\text{cm}^{-1}$), binding energy ($D_0 = 806.4\,\text{cm}^{-1}$ vs. $D_0 = 808.2\,\text{cm}^{-1}$), and the equilibrium bond length ($R_e = 2.435$ Å vs. $R_e = 2.445 \pm 0.005$ Å). The vibrational energy terms are on average only 0.8 cm^{-1} away from the latest experimental results showing that the spectroscopic accuracy is achieved. No deterioration of the results is observed for higher vibrational levels indicating that a balanced description of the potential energy curve for all internuclear distances is obtained. We confirm the existence of the last (twelfth) vibrational state and predicted that it lies just 0.4 cm^{-1} below the onset of the continuum. Lastly, this study proves that the Slater-type orbitals can routinely be used as a basis set for quantum-chemical calculations for diatomic systems.

Ab initio interaction energy curve for the ground state of beryllium dimer

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This work concerns with *ab initio* calculations of the complete potential energy curve for the $X^1\Sigma_g+$ state of the beryllium dimer - a continuation of our previous work on this topic [M. Lesiuk *et al.*, Phys. Rev. A **91**, 012510 (2015)]. High accuracy of the computations is one of the primary goals of the paper and is achieved with the help of high-order electronic structure methods and large Slater-type orbitals basis sets. Several small physical effects due to, e.g. relativity and quantum electrodynamics, are included in the theoretical description. Influence of the finite nuclear mass corrections (non-Born-Oppenheimer effects) is completely negligible at present. The theoretically determined well-depth ($D_e = 933.3 \pm 2.5\text{cm}^{-1}$) and the dissociation energy ($D_0 = 806.4\,\text{cm}^{-1}$) are in a very good agreement with the most recent empirical data. We also confirm the existence of the weakly bounded twelfth vibrational level and predict that it lies just 0.4 cm^{-1} below the onset of the continuum.

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I. INTRODUCTION

In the past several decades beryllium dimer has been a subject of many scientific studies, both experimental and theoretical. The first works predicted the interaction between two closed-shell beryllium atoms to be purely repulsive [1], even when the electron correlation effects were partially included [2]. However, more sophisticated quantum chemistry methods became available in the late 70' and early 80' allowing to re-evaluate the scientific consensus about the nature of the beryllium dimer [3–5]. It was predicted that this molecule is bound, albeit very weakly, with some similarities to the noble gas dimers.

Further improvements in the theoretical description of the beryllium dimer were presented by Liu and McLean [6], and somewhat later by Harrison and Handy [7]. Both studies reported that the single and double excitations with respect to the single reference wavefunction are not sufficient to describe the bonding correctly. Inclusion of triple and quadruple excitations (either by means of full CI or multireference CI methods [8–10]) is necessary to obtain more quantitative results. This allowed to revise the bonding energy up to several hundreds of cm^{-1}. Moreover, it was shown that the pathological behaviour of this system is largely due to near-degeneracy of the $2s$ and $2p$ energy levels. Since then, these conclusions have been confirmed by several other authors [11–18].

The fact that the beryllium dimer is an apparently simple yet challenging system have made it frequently studied in the literature. The present consensus is that the binding energy of the beryllium dimer is in the range $920-940$ cm^{-1} and the bond length is approximately 2.44Å. The reported values differ depending on the employed level of theory but it appears that the most reliable theoretical results to date were given by Martin [20] (944 ± 25 cm^{-1}), Røggen and Veseth [21] (945 ± 15 cm^{-1}), Patkowski et al. [22] (938 ± 15 cm^{-1}), Koput [23] (935 ± 10 cm^{-1}), and the present authors [24] (929 ± 1.9 cm^{-1}). Other notable papers are Refs. [25–29] and a more detailed older bibliography is found in Refs. [21, 22]. Semiempirical (or morphed) potentials have also been constructed for this system [33, 37].

Experimental studies of the beryllium dimer ground state also have a long history. The first experimental works of Bondybey et al. [30–32] were conducted in the middle 80' and only several vibrational levels were observed. These incomplete data and a lacking theoretical model led to a considerably underestimated value for the well-depth, 790 ± 30 cm^{-1}. This prediction was later revised by Spirko [33] who combined the experimental results of Bondybey et al. [30–32] with portions of theoretical potentials and recommended a new value of 923 cm^{-1}.

A refined experiment was performed in 2009 by Merritt et al. [34] who reported 929.7 ± 2 cm^{-1} for the well-depth. In addition to that, eleven vibrational levels were characterised [35]. However, to extract the potential parameters (well-depth, equilibrium distance, etc.) from the experimental results, Merritt et al. [34] employed a relatively simple Morse-like potential. It vanishes too quickly (i.e. exponentially) at large internuclear distances. This deficiency was corrected by Patkowski et al. [36] who calculated a theoretical potential energy curve with the correct C_6/R^6 long-range behaviour. This potential was not accurate enough to reproduce the experimental results with the spectroscopic accuracy, but by a simple morphing (i.e. scaling) of the potential the accuracy was improved greatly. By introducing two empirical parameters they reproduced the experimental vibrational levels to within 1.0 cm^{-1}. Five empirical parameters give a potential accurate to within 0.1 cm^{-1}.

Even more interestingly, the morphed potential of Patkowski et al. [36] supported an additional (i.e. twelfth) vibrational level. This level was not originally

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reported in the experimental paper of Merritt et al. [34] and its existence came quite as a surprise. Several subsequent works tired to reproduce the observations of Patkowski et al. [36] without resorting to any empirical adjustments [23]. In parallel, refined direct-potential-fit analyses provided improved (albeit purely empirical) potentials [37], supporting the findings of Ref. [36].

In this paper we expand upon our previous work [24] where the interaction energy of the beryllium dimer has been determined with help of the Slater-type orbitals [40, 41] by using the newly developed programs [38, 39]. We refine slightly the results given previously [24] and calculate the full potential energy curve (PEC) including corrections due to relativistic, adiabatic, etc. effects. Next, we generate analytic fits of the interaction potentials and solve the nuclear Schrödinger equation to obtain the vibrational energy terms. Finally, an extensive comparison with theoretical and experimental values of other authors is given.

Atomic units are used throughout the paper unless explicitly stated otherwise. We adopt the following conversion factors and fundamental constants: $1\,a_0 = 0.529\,177$Å (Bohr radius), $1\,\mathrm{u} = 1822.888$ (unified atomic mass unit), $1\,\mathrm{a.u.} = 219\,474.63\ \mathrm{cm}^{-1}$ (wavenumbers), $\alpha^{-1} = 137.035\,999\,139$ (the fine structure constant). These values are in line with the recent CODATA recommendations [42]. We assume that the mass of the only stable isotope of beryllium (^{9}Be) is $m(\mathrm{Be}) = 9.0121\,831\,\mathrm{u}$ which is the latest experimental value [43]. All data presented in this paper refer to the ^{9}Be isotope. We also adopt a convention that interaction energies are positive whenever the underlying interactions are attractive.

II. *AB INITIO* CALCULATIONS

A. Basis sets

In this work we use basis sets composed of the canonical Slater-type orbitals [40, 41]

$$\chi_{lm}(\mathbf{r};\zeta) = \frac{(2\zeta)^{n+1/2}}{\sqrt{(2n)!}}\, r^l e^{-\zeta r}\, Y_{lm}(\theta,\phi), \qquad (1)$$

where $\zeta > 0$ is a nonlinear parameter to be optimised, and Y_{lm} are spherical harmonics in the Condon-Shortley phase convention. For brevity, the functions (1) with $l = 0$ are called the s-orbitals, $l = 1$ - p-orbitals *etc.* In our previous paper [24] the optimisation of the STOs basis sets has been described in fine details. It the present work we employ slightly modified procedures, so let us describe the most important differences. First, instead of the conventional well-tempering of the nonlinear parameters for a given angular momentum (ζ_{lk}) we employ a more flexible formula

$$\zeta_{lk} = \alpha_l\, \beta_l^{k+\gamma_l k^2} \quad \text{with} \quad k = 0, 1, 2, \ldots \qquad (2)$$

TABLE I. Composition of the STO basis sets for the beryllium atom used in this work.

l	valence	core	diffuse
2	$7s2p1d$	$1s1p$	$1s1p1d$
3	$8s3p2d1f$	$2s2p1d$	$1s1p1d1f$
4	$9s4p3d2f1g$	$2s3p2d1f$	$1s1p1d1f1g$
5	$9s5p4d3f2g1h$	$3s4p3d2f1g$	$1s1p1d1f1g1h$
6	$9s6p5d4f3g2h1i$	$3s5p4d3f2g1h$	$1s1p1d1f1g1h1i$

where α_l, β_l, and γ_l are free parameters to be optimised. For a brief discussion of advantages of this expansion see Ref. [44].

Similarly as in the previous works we divide the basis sets into the core and valence components and employ the correlation-consistency principle [45] to determine the final composition of both parts. However, in contrast to Ref. [24] an additional set of diffuse functions is added to each basis. Therefore, all basis sets used here are doubly augmented. The low-exponent functions are especially beneficial for larger internuclear distances. The final composition of all basis sets is given in Table I. Other details can be obtained from the authors upon request. For brevity, the valence-only basis sets are denoted shortly wtcc-l whilst the core-valence basis sets are abbreviated tc-wtcc-l. In both cases, l is the highest angular momentum present in the basis set and the double augmentation is denoted with the prefix da-, e.g. da-wtcc-l.

In Table II we present results of the FCI calculations for the beryllium atom in the da-tc-wtcc-l basis sets. The Hartree-Fock (HF) limit is reached already with the basis set $l = 5$ and we do not attempt to extrapolate the HF results. The correlation energies are extrapolated with the help of the following two-point formula [46]

$$E = a + b\,(l+1)^{-3} + c\,(l+1)^{-5}, \qquad (3)$$

where l is the highest angular momentum present in the basis, and the parameters a, b, c are obtained by least-squares fitting. Special basis sets are used further in the paper for calculation of the relativistic and QED effects. In this case we modify the original da-tc-wtcc-l basis sets by replacing all s-type functions by a common set of twelve $1s$ orbitals. This set has been obtained by minimising the Hartree-Fock energy of the beryllium atom.

B. Four-electron (valence) contribution

Within the current computational capacities the full CI (FCI) method cannot be used for eight-electron systems with any reasonable basis set. Therefore, in the present work we rely on a composite scheme where the total interaction energy is divided into a set of well-defined components of different magnitudes. The largest components are calculated the most accurately, i.e. employing larger

TABLE II. The total nonrelativistic ($E_{\rm total}$) and correlation energies ($E_{\rm c}$) of the beryllium atom at the FCI level of theory (see the main text for details). The limit of the Hartree-Fock energy is −14.573 023 a.u. The second column denotes the total number of STOs basis set functions (N) for a given angular momentum l. All values are given in the atomic units.

l	N	$E_{\rm c}$ / mH	$E_{\rm total}$
2	31	−85.976	−14.658 998
3	67	−91.479	−14.664 502
4	124	−92.994	−14.666 017
5	204	−93.608	−14.666 631
6	316	−93.902	−14.666 925
CBS	∞	–	–
Ref. [67]		−0.094 333	−14.667 356

TABLE III. Four-electron valence calculations for the beryllium dimer; l is the basis set cardinal number, N_b is the number of basis set functions, $E_{\rm int}^{\rm HF}$ and $E_{\rm int}^{\rm FCI}$ are interaction energies calculated at the Hartree-Fock and FCI levels of theory, respectively. Results are given for two internuclear distances, R. Interaction energies are given in wavenumbers, cm^{-1}, and internuclear distances in Bohrs.

l	N_b	$R = 4.75$		$R = 8.00$	
		$E_{\rm int}^{\rm HF}$	$E_{\rm int}^{\rm FCI}$	$E_{\rm int}^{\rm HF}$	$E_{\rm int}^{\rm FCI}$
2	54	−2367.5	270.3	−124.5	116.2
3	110	−2324.3	692.2	−123.5	155.0
4	192	−2320.6	804.8	−123.3	167.7
5	302	−2320.5	831.7	−123.2	171.1
6	448	−2320.4	842.7	−123.2	172.0
∞	∞	−2320.4 ± 0.1	868.6 ± 1.6	−123.2 ± 0.1	175.4 ± 1.2

basis sets or more reliable electronic structure methods. Smaller contributions are treated at a more approximate level of theory or even completely neglected. This saves a huge portion of the computational time.

It is well-known that the dominant contribution to the interaction energy of the beryllium dimer comes from four valence electrons. In fact, by freezing 1s core orbitals of both atoms one can still recover approximately 90% of the total interaction energy. Unfortunately, calculation of the valence four-electron contribution is very problematic due to 2s-2p near-degeneracy of the energy levels in beryllium. This property leads to a significant multireference character of the dimer. As a result, CCSD and even CCSDT methods should not be used to calculate the valence four-electron contribution to the interaction energy. To get a quantitative answer one has to use either the FCI method or some multireference CI/CC variant. In the present paper we choose the former option, mostly because of its black-box character and no arbitrariness, e.g. in selection of the active orbitals space.

Valence four-electron FCI interaction energies were calculated with the basis sets da-wtcc-l, $l = 2 - 6$. This was accomplished by using the FCI program HECTOR [47] written by one of us (MP). Canonical Hartree-Fock orbitals generated by external programs were used as a starting point for the FCI iterations. All FCI computations were performed utilising the D2h Abelian point group symmetry. Basis set superposition error is eliminated by applying the counterpoise correction [48]. Parenthetically, the largest basis set leads to a FCI matrix of dimension over one billion (10^9). In Table III we present exemplary results of the valence FCI calculations. To provide a broader picture we list these data for two interelectronic distances: $R = 4.75$ is located near the minimum of PEC and $R = 8.0$ is already close to the van der Waals region.

To reach the basis set limit of the calculated quantities and estimate the corresponding errors we rely on CBS extrapolations. The only exception is the Hartree-Fock (HF) energy - one can see from Table III that the HF contribution to the interaction energy is converged to better than 0.1 cm^{-1} already in the basis set $l = 6$. Therefore, we simply take the value obtained with $l = 6$ as the HF limit. The error of this approximation is negligible in the present context. A more complicated situation is found for the contributions coming from the correlation energy. To extrapolate them we employ the same formula which has been demonstrated to give reliable results for an isolated atom, Eq. (3). Overall, we find that the curve (3) fits the raw data points reasonably well. The extrapolated values of the interaction energy are also listed in Table III.

Let us also illustrate how important the post-CCSD(T) effects are in calculation of the valence contributions to the interaction energy. For example, the interaction energy calculated with the frozen-core CCSD(T) method [49] and the $l = 6$ basis set is 623.9 cm^{-1} for $R = 4.75$ and 59.6 cm^{-1} for $R = 10.0$. Comparison with the values calculated at the FCI level of theory (cf. Table III) shows that CCSD(T) is capable of reproducing only about 75% of the total valence interaction energy for $R = 4.75$ and 90% for $R = 10.0$. These deviations cannot be attributed to the basis set incompleteness error since a very similar picture is obtained from the CBS-extrapolated data. Therefore, the CCSD(T) method alone is not a reasonable level of theory for calculation of the valence contribution to the interaction energy of the beryllium dimer.

C. Core-core and core-valence contributions

Let us now consider a contribution to the total interaction energy coming from the core-core and core-valence (i.e. inner-shell) correlations, $E_{\rm int(core)}$. It is defined simply as a difference between the exact nonrelativistic BO interaction energy and the exact four-electron valence contribution. Fortunately, calculation of this contribu-

TABLE IV. Core-core and core-valence contributions ($E^{\rm X}_{\rm int,core}$) to the interaction energy of the beryllium dimer calculated at various levels of theory (X) in the da-tc-wtcc-l basis sets (see the main text for precise definitions of all quantities); N_b is the number of basis set functions. Interaction energies are given in wavenumbers, $\rm cm^{-1}$, and internuclear distances in Bohrs.

l	N_b	$R = 4.75$			$R = 8.00$		
		$E^{\rm CCSD(T)}_{\rm int,core}$	$\Delta E^{\rm T}_{\rm int,core}$	$\Delta E^{\rm (Q)}_{\rm int,core}$	$E^{\rm CCSD(T)}_{\rm int,core}$	$\Delta E^{\rm T}_{\rm int,core}$	$\Delta E^{\rm (Q)}_{\rm int,core}$
2	54	26.1	−7.4	1.0	+0.2	−0.8	+0.4
3	110	50.7	−4.5	0.6	−1.1	−0.8	+0.5
4	192	54.1	−3.2	—	−1.6	—	—
5	302	54.8	—	—	−1.7	—	—
∞	∞	55.4 ± 0.6	-2.0 ± 0.4	0.4 ± 0.2[a]	-1.9 ± 0.2	-0.8 ± 0.4[a]	$+0.6 \pm 0.3$[a]

[a] obtained by a two-point extrapolation

tion is somewhat simpler than in case of the valence effects. The biggest contribution to $E_{\rm int(core)}$ can be obtained with help of the the CCSD(T) method, $E^{\rm CCSD(T)}_{\rm int(core)}$. The post-CCSD(T) contributions to $E_{\rm int(core)}$ constitute only a few percents of the exact value - a stark contrast to the previous case of $E^{\rm FCI}_{\rm int}$.

In Table IV we present the inner-shell contributions to the interaction energy ($E^{\rm X}_{\rm int,core}$) calculated at several different levels of theory, X. In this work we consider X to be either CCSD(T), CCSDT or CCSDT(Q). For convenience, we also define some relative quantities

$$\Delta E^{\rm T}_{\rm int,core} = E^{\rm CCSDT}_{\rm int(core)} - E^{\rm CCSD(T)}_{\rm int(core)}, \quad (4)$$

$$\Delta E^{\rm (Q)}_{\rm int,core} = E^{\rm CCSDT(Q)}_{\rm int(core)} - E^{\rm CCSDT}_{\rm int(core)}, \quad (5)$$

Calculation of the above two post-CCSD(T) corrections is very computationally intensive. For example, single-point CCSDT calculations for the dimer in the $l = 4$ basis take about a month with our computational resources. The cost of the CCSDT(Q) method is even larger which effectively prohibits the use of basis sets other than $l = 2, 3$. In the case of the CCSDT method we managed to perform calculations up to $l = 4$ only for several points of PEC, namely $R = 4.0 - 5.5$. This is the region where the interaction energy is the largest and the inner-shell corrections are the most important on the relative basis. In fact, for $R = 4.75$ the inner-shell contributions stand for about 8% of the total interaction energy in the BO approximation (cf. Table III). For $R = 8.0$ this ratio drops to less than 2%.

Extrapolations of the CCSD(T) results to the CBS limit are performed with help of the formula (3) with $l = 2-5$. The error is estimated as a differences between the value calculated with the biggest basis set and the extrapolated limit. The same technique is used for the CCSDT method when results from $l = 2, 3, 4$ basis sets are available. The error is estimated as 20% of the corresponding value. For the remaining data (i.e. where results only from $l = 2, 3$ basis sets are available) we extrapolate the results by using the two-point formula. Clearly, this approach is not as reliable as the other estimations employed in this work and thus we assign an uncertainty of 50% to the values calculated in this way. Fortunately, the two-point extrapolations have to be performed only for $R > 5.5$ where the post-CCSD(T) contributions are relatively small. Therefore, even if the estimated limits of the T and T(Q) contributions were wrong by a factor of 50% the overall quality of the results would be affected only marginally.

Parenthetically, a typical way to estimate the post-CCSD(T) contributions is to evaluate them is some small basis set and add this value to the final results. As can be seen in Table IV, this is not a particularly reasonable approach in the present context. In fact, smaller basis sets (i.e. $l = 2, 3$) tend to grossly overestimate the post-CCSD(T) effects, sometimes even by a factor of 3 or so.

The final error of the core-core and core-valence contributions to the interaction energy is obtained by summing squares of the errors of all constituents ($E^{\rm CCSD(T)}_{\rm int,core}$, $\Delta E^{\rm T}_{\rm int,core}$, $\Delta E^{\rm (Q)}_{\rm int,core}$) and taking the square root. For example, this gives us the total value of $E_{\rm int(core)} = 53.8 \pm 0.7\,\rm cm^{-1}$ for $R = 4.75$ and $E_{\rm int(core)} = -2.1 \pm 0.5\,\rm cm^{-1}$ for $R = 8.0$.

D. Relativistic corrections

To meet the high accuracy requirements of this study we must incorporate in our description of the interaction potential the subtle effects of relativity. As long as the constituting elements are not too heavy, the leading-order relativistic corrections to the molecular energy levels can be calculated by perturbation theory. The approach based on the Breit-Pauli Hamiltonian [50] is particularly complete

$$E^{(2)} = \langle P_4 \rangle + \langle D_1 \rangle + \langle D_2 \rangle + \langle B \rangle, \quad (6)$$

$$\langle P_4 \rangle = -\frac{\alpha^2}{8} \langle \sum_i \nabla_i^4 \rangle, \quad (7)$$

TABLE V. Relativistic corrections to the interaction energy of the beryllium dimer calculated in the da-tc-wtcc-l basis sets augmented with a universal set of 1s functions. The column "valence" gives results calculated at the valence FCI level of theory and the column "core" provides the inner-shell corrections (see the main text for details). The core correction is neglected for the two-electron Darwin and Breit terms. Interaction energies are given in wavenumbers, cm^{-1}, and internuclear distances in Bohrs.

l	$\langle P_4\rangle$		$\langle D_1\rangle$		total	$\langle D_2\rangle$	$\langle B\rangle$	total
	valence	core	valence	core	Cowan-Griffin			Breit-Pauli
				$R = 4.75$				
2	−14.1	−0.40	10.4	0.31	−3.8	0.39	−0.69	−4.1
3	−15.2	−0.55	11.2	0.43	−4.1	0.43	−0.71	−4.4
4	−15.4	−0.57	11.3	0.44	−4.2	0.44	−0.72	−4.5
∞	-15.6 ± 0.2	-0.60 ± 0.03	11.5 ± 0.2	0.47 ± 0.03	-4.2 ± 0.3	0.49 ± 0.05[a]	-0.75 ± 0.03[a]	-4.5 ± 0.3
				$R = 8.00$				
2	−0.26	−0.006	0.19	0.002	−0.07	0.009	−0.016	−0.08
3	−0.39	−0.008	0.28	0.003	−0.12	0.013	−0.017	−0.12
4	−0.43	−0.009	0.30	0.004	−0.14	0.015	−0.017	−0.14
∞	-0.45 ± 0.02	-0.01 ± 0.001	0.32 ± 0.02	0.005 ± 0.001	-0.14 ± 0.03	0.020 ± 0.005[a]	-0.018 ± 0.001[a]	-0.14 ± 0.03

[a] the error estimation includes the uncertainty due to the neglected core contribution

$$\langle D_1\rangle = \frac{\pi}{2}\alpha^2 \sum_a Z_a \langle \sum_i \delta(\mathbf{r}_{ia})\rangle, \tag{8}$$

$$\langle D_2\rangle = \pi\alpha^2 \langle \sum_{i>j} \delta(\mathbf{r}_{ij})\rangle, \tag{9}$$

$$\langle B\rangle = \frac{\alpha^2}{2} \langle \sum_{i>j} \left[\frac{\nabla_i \cdot \nabla_j}{r_{ij}} + \frac{\mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_j)\nabla_i}{r_{ij}^3} \right]\rangle, \tag{10}$$

where i and a denote electrons and nuclei, respectively, and $\langle \hat{\mathcal{O}}\rangle$ is the expectation value of an operator $\hat{\mathcal{O}}$. Further in the paper the above corrections are referred shortly as the mass-velocity, one-electron Darwin, two-electron Darwin, and orbit-orbit terms (in the order of appearance). Moreover, the sum of $\langle P_4\rangle$ and $\langle D_1\rangle$ terms is sometimes called the Cowan-Griffin correction [51], and the names "orbit-orbit" and "Breit" shall be used interchangeably for the term (10).

In calculation of the relativistic effects we adopt the following approach. The relativistic contributions are divided into the valence and core components. In the case of the two-electron relativistic corrections [$\langle D_2\rangle$ and $\langle B\rangle$] we neglect the core contribution. This is justified because the two-electron contributions are by an order of magnitude smaller than $\langle P_4\rangle$ and $\langle D_1\rangle$ terms, and the core components are further by an order of magnitude smaller than the valence effects. We estimated that the neglected terms would bring a contribution of only about 0.01 cm^{-1} to the interaction energy at the minimum of PEC. Thus, they are entirely negligible in the present study, cf. Ref. [24]. Nonetheless, we add an additional uncertainty of 5% to the calculated two-electron relativistic effects due to the neglected core contributions.

Extrapolations of the relativistic corrections to the complete basis set limit are performed with help of Eq. (3). The only exception is the two-electron Darwin term where we found the L^{-1} convergence pattern. This is consistent with the numerical experience of Refs. [52, 53] and theoretical findings of Kutzelnigg [54]. In all cases the errors are estimated as a difference between the extrapolated result and the value in the largest basis set.

The valence relativistic corrections are in all cases evaluated with help of the FCI method. The core corrections to the $\langle P_4\rangle$ and $\langle D_1\rangle$ terms were computed at the CCSD(T) level of theory. In Table V we show a short summary of the results for two interelectronic distances. One can see than in both cases the relativistic contribution to the interaction energy is non-negligible. Close to the minimum of PEC the relativistic effects decrease the interaction energy by about 5 cm^{-1} (or 0.5%) - a surprisingly large amount for a system as light as the beryllium dimer.

E. Other corrections

Let us now pass to the calculation of the QED effects. According to the so-called nonrelativistic QED theory the leading-order post-Breit-Pauli correction to the energy of a molecule in a singlet spin state reads [55–57]

$$E^{(3)} = E_1^{(3)} + E_2^{(3)} + \langle H_{AS}\rangle, \tag{11}$$

TABLE VI. QED corrections to the interaction energy of the beryllium dimer calculated in the da-tc-wtcc-l basis sets augmented with a universal set of $1s$ functions. The core corrections are neglected. Interaction energies are given in wavenumbers, cm^{-1}, and internuclear distances in Bohrs.

l	$E_1^{(3)}$	$E_2^{(3)}$	$\langle H_{AS}\rangle$	total QED
		$R = 4.75$		
2	0.31	−0.011	−0.012	0.29
3	0.34	−0.012	−0.013	0.32
4	0.34	−0.012	−0.014	0.32
∞	0.35 ± 0.01	-0.014 ± 0.002	-0.020 ± 0.007	0.32 ± 0.02
		$R = 8.00$		
2	−0.006	0.0[a]	0.0[a]	−0.006
3	−0.008	0.0[a]	0.0[a]	−0.008
4	−0.009	0.0[a]	0.0[a]	−0.009
∞	-0.009 ± 0.001	0.0[a]	0.0[a]	-0.009 ± 0.001

[a]below 10^{-3} cm^{-1}; impossible to calculate reliably due to large cancellations between the dimer and the monomers

where $E_1^{(3)}$ and $E_2^{(3)}$ are the one- and two-electron contributions, respectively

$$E_1^{(3)} = \frac{8\alpha}{3\pi}\left(\frac{19}{30} - 2\ln\alpha - \ln k_0\right)\langle D_1\rangle, \tag{12}$$

$$E_2^{(3)} = \frac{\alpha}{\pi}\left(\frac{164}{15} + \frac{14}{3}\ln\alpha\right)\langle D_2\rangle, \tag{13}$$

and $\langle H_{AS}\rangle$ is the Araki-Sucher correction given by the formula

$$\langle H_{AS}\rangle = -\frac{7\alpha^3}{6\pi}\langle\sum_{i>j}\hat{P}\left(r_{ij}^{-3}\right)\rangle, \tag{14}$$

where $\hat{P}\left(r_{ij}^{-3}\right)$ denotes the regularised r_{ij}^{-3} distribution,

$$\langle\hat{P}\left(r_{ij}^{-3}\right)\rangle = \lim_{a\to 0}\langle\theta(r_{ij}-a)\, r_{ij}^{-3} + 4\pi\left(\gamma_E + \ln a\right)\delta(\mathbf{r}_{ij})\rangle, \tag{15}$$

and $\gamma_E \approx 0.57722$ is the Euler-Mascheroni constant. The other new quantity appearing in the above expressions is the Bethe logarithm [50, 58], $\ln k_0$.

Let us note that the Araki-Sucher term is formally a two-electron expectation value so it could have been included in $E_2^{(3)}$. However, we prefer to consider it separately due to its unique nature. Additionally, it may be slightly confusing that the name "one-electron correction" is assigned to $E_1^{(3)}$ as $\ln k_0$ is a many-electron quantity. However, this establishes a close parallel between the QED and relativistic corrections, cf. Eqs. (6)-(10).

Calculation of the complete leading-order QED corrections for many-electron molecules is notoriously difficult. This is due to presence of two complicated terms: $\langle H_{AS}\rangle$ and $\ln k_0$. A general method to evaluate the Araki-Sucher correction with the help of the standard quantum chemistry methods has been presented only very recently [59]. This approach has been used in the present paper. Similarly as for the two-electron relativistic corrections we neglect the core contributions to the $\langle H_{AS}\rangle$ term.

Even more complicated issue is evaluation of the Bethe logarithm, $\ln k_0$. Fortunately, in all molecules where the Bethe logarithm is known accurately (hydrogen molecular ion [60–63], hydrogen molecule [64–66] and several others) $\ln k_0$ depends weakly on the internuclear distance, R. Therefore, as long as one is not interested in the interaction potential for a very small R, the atomic value of $\ln k_0$ can be adopted. The Bethe logarithm for the beryllium atom has been evaluated recently by Pachucki and Komasa [68], $\ln k_0 = 5.75034$.

With the help of this approximation $E_1^{(3)}$ and $E_2^{(3)}$ are calculated by a simple scaling of the $\langle D_1\rangle$ and $\langle D_2\rangle$ corrections. The scaling factors do not depend on R and in the present case are approximately equal to 0.0293 and −0.0279 for $E_1^{(3)}$ and $E_2^{(3)}$, respectively. In Table VI we present values of all QED corrections for $R = 4.75$ and $R = 8.00$. They were calculated with the same basis sets as the relativistic effects. The total QED correction is only by an order of magnitude smaller than the Breit-Pauli contribution. This is somewhat contradictory to the estimations based on the order in α.

The one-electron term $E_1^{(3)}$ dominates the total QED correction and the two-electron effects are smaller by a factor of 20−30. Interestingly, the total QED contribution (12) increases the interaction energy of the beryllium dimer at every point of PEC. Unfortunately, for larger R we have encountered significant difficulties in calculation of the two-electron QED effects. This is mostly due to the fact that they are very small ($< 10^{-3}$ cm^{-1}) and subtraction between the dimer and monomer values leads to

a large cancellation of significant digits (cf. Table VI). Therefore, further in the text we neglect the two-electron QED effects and include only the $E_1^{(3)}$ term as the dominant contribution to the interaction energy.

We can also estimate the influence of the higher-order QED effects on the total interaction energy of the beryllium dimer. Experiences from the helium atom [69, 70] and from the hydrogen molecule [71] suggest that the dominant term of the α^4 QED correction is the so-called one-loop diagram [72]. It is given by a simple formula

$$E^{(4)}_{\rm one-loop} = 16\alpha^2 \left(\frac{427}{192} - \ln 2\right) \langle D_1 \rangle, \qquad (16)$$

for a molecule in singlet electronic state. Since the one-electron Darwin term $\langle D_1 \rangle$ has already been calculated in the course of this work, the one-loop term is straightforward to obtain. We find that it contributes as little as about $0.02\,\mathrm{cm}^{-1}$ near the minimum of PEC. Therefore, the higher-order QED effects can be safely neglected within the present accuracy standards, but one can rest assured that the NRQED perturbative series is sufficiently well-converged already in the third-order.

Finally, we consider the finite nuclear mass effects. As it is well-known, the leading-order finite nuclear mass correction to the energy of a molecule is the so-called adiabatic correction (also known as the diagonal Born-Oppenheimer correction). As indicated in several previous works [23, 24], this correction is rather small in the present case and we calculate it at the CCSD level of theory [73]. For this purpose we employ the Gaussian-type orbitals (GTOs) basis developed by Prascher et al [74]. Note that this is the only element of our calculations where we resort to GTOs. Our results indicate that the adiabatic effects are indeed very small for the ground state of the beryllium dimer. For example, they amount only to $-0.14\,\mathrm{cm}^{-1}$ and $-0.02\,\mathrm{cm}^{-1}$ for $R = 4.75$ and $R = 8.0$, respectively. This justifies the omission of the post-Born-Oppenheimer effects further in the paper.

The influence of various minor physical effects on the interaction energy of the beryllium dimer is illustrated in Fig. 1. By the term "minor" we mean all non-negligible contributions calculated in the course of this work other than the four-electron FCI and the inner-shell CCSD(T) contributions (which together constitute about 99% of the total value). Overall, the one-electron relativistic corrections are the most important among the quantities included in Fig. 1, followed by the inner-shell post-CCSD(T) effects. The remaining corrections shown in Fig. 1 are by an order of magnitude smaller than the latter two. An interesting feature visible in Fig. 1 is a pronounced hump in the inner-shell post-CCSD(T) corrections curve. We believe that this feature is related to the change in the character of the bonding phenomena as argued in Ref. [18].

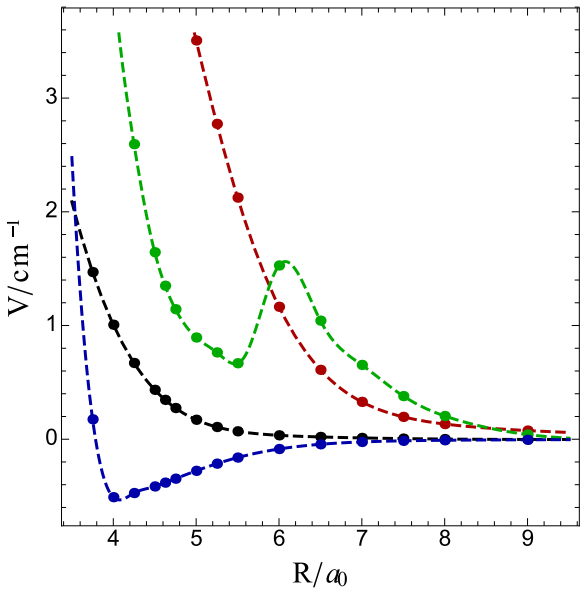

FIG. 1. Minor corrections to PEC of the beryllium dimer as a function of the internuclear distance. By red, black, green, and blue colors we denote, respectively, the one-electron relativistic correction, two-electron relativistic correction, post-CCSD(T) inner-shell correction, and one-electron QED correction.

F. Computational details

Most of the electronic structure calculations described above were carried out with help of the GAMESS program suite [75, 76]. The only exceptions are the FCI calculations (accomplished with HECTOR program [47]), higher-

TABLE VII. Optimised parameters of the fit (17) for the Born-Oppenheimer potential $[V^{\rm BO}(R)]$. All values are given in the atomic units. The symbol $X[\pm n]$ stands for $X \cdot 10^{\pm n}$. Not all digits reported are significant.

parameter	$V^{\rm BO}(R)$	parameter	$V^{\rm BO}(R)$
a	+6.00 000[−01][a]	C_6	+2.14 000[+02][b]
b	+5.00 000[−02][a]	C_8	+1.02 300[+04][b]
η	+6.00 000[−01][a]	C_{10}	+5.16 500[+05][b]
c_0	−6.91 469[+04]	c_7	+1.64 811[+02]
c_1	+1.36 564[+05]	c_8	−1.69 778[+01]
c_2	−1.22 785[+05]	c_9	+1.27 595[+00]
c_3	+6.65 299[+04]	c_{10}	−6.79 905[−02]
c_4	−2.42 326[+04]	c_{11}	+2.43 225[−03]
c_5	+6.26 405[+03]	c_{12}	−5.23 504[−05]
c_6	−1.18 199[+03]	c_{13}	+5.11 965[−07]

[a] fixed [b] taken from Ref. [81]

order coupled cluster methods (ACESII [77]) and calculations of the adiabatic correction (CFOUR [78]). Matrix elements of the orbit-orbit and Araki-Sucher operators were not evaluated directly in the STOs basis, but with help of the Gaussian fitting technique by using twelve GTOs representing a single exponential orbital. For a single point of the curve ($R = 4.75$) we recomputed all quantities employing fifteen GTOs but the changes were marginal.

To create a complete PEC we selected the following grid of internuclear distances

$$\begin{aligned}
&\text{from } R = 3.5 \text{ to } R = 5.5 \text{ in steps of } 0.25,\\
&\text{from } R = 5.5 \text{ to } R = 8.0 \text{ in steps of } 0.50,\\
&\text{from } R = 8.0 \text{ to } R = 15.0 \text{ in steps of } 1.0,\\
&\text{from } R = 15.0 \text{ to } R = 25.0 \text{ in steps of } 2.5,
\end{aligned}$$

in the atomic units. Additionally, we evaluated a single point at $R = 4.625$ to improve the description of the minimum of PEC. This gives a total number of 26 points with increasing spacings, so that the grid is more dense in regions with larger variations of the total interaction energy.

III. ANALYTIC FITS OF THE POTENTIALS

The raw *ab initio* data points were fitted with the conventional analytic form frequently used for atom-atom interactions

$$V(R) = e^{-aR-bR^2} \sum_{k=0}^{N_p} c_k R^k - \sum_{n=3}^{N_a} f_{2n}(\eta R)\, \frac{C_{2n}}{R^{2n}}, \quad (17)$$

where $f_{2n}(\eta R)$ are the Tang-Toennies damping functions [79]. This expression contains three nonlinear parameters (a, b, and η) and an adjustable number of linear parameters (N_p) and asymptotic constants (N_a). In the case of the BO potential we employ the asymptotic constants C_{2n} evaluated with more accurate theoretical methods. For the C_6, C_8, and C_{10} dispersion coefficients we adopt the values reported by Porsev and Derevianko [80, 81] which are in a very good agreement with the earlier results of Mitroy and Bromley [82]. No reliable data is available for the higher-order constants so they are neglected here. Unfortunately, the BO data is very difficult to fit with a smooth function in the form (17). This is clearly related to the usual shape of this curve illustrated in Fig. 2. We needed as many as 14 parameters to obtain an accurate fit of the BO potential. The optimised values are given in Table VII. Further work is necessary to reduce the number of parameters.

The generic formula (17) is used also for fitting of the relativistic corrections. Each correction defined by Eq. (6) is fitted separately. Unfortunately, we are not aware of any reliable asymptotic constants which could be used for the present purposes. Therefore, we use Eq. (17) with $N_p = 2$ and $N_a = 3$ and obtain approximate dispersion coefficients directly from the fit. This leaves nine free parameters to be determined by the fitting procedure. The only exception from the procedure described above is found for the orbit-orbit correction, Eq. (10). It possesses an usual C_4/R^4 long-range asymptotics. Therefore, instead of the $C_6 - C_{10}$ coefficients we use leading-order $C_4 - C_8$ as free parameters. The one-electron QED correction is obtained by scaling the fit of the $\langle D_1 \rangle$ relativistic correction according to the formula (12). The fitting errors are by an order of magnitude smaller than the estimated uncertainties of the respective theoretical results. The final optimised values of the fitting parameters are given in Tables VIII and IX and the complete PEC is illustrated in Fig. 2.

TABLE VIII. Optimised parameters of the fit (17) for the one-electron relativistic corrections, see Eqs. (7) and (8) for the definitions. All values are given in the atomic units. The symbol $X[\pm n]$ stands for $X \cdot 10^{\pm n}$.

parameter	$V^{\mathrm{P4}}(R)$	$V^{\mathrm{D1}}(R)$
a	+5.71 363[−01]	+5.39 086[−01]
b	+6.97 996[−02]	+7.51 463[−02]
η	+1.70 542[+00]	+1.17 979[+00]
c_0	+3.16 587[−01]	−2.11 563[−02]
c_1	−1.35 137[−02]	+9.08 454[−03]
c_2	+1.30 996[−03]	−8.64 036[−04]
C_6	+4.10 578[−01]	−2.71 691[−01]
C_8	+6.40 639[+01]	−4.37 072[+01]
C_{10}	−2.90 822[+03]	+1.78 582[+03]

TABLE IX. Optimised parameters of the fit (17) for the two-electron relativistic corrections, see Eqs. (9) and (10) for the definitions. All values are given in the atomic units. The symbol $X[\pm n]$ stands for $X \cdot 10^{\pm n}$.

parameter	$V^{\mathrm{D2}}(R)$	$V^{\mathrm{B}}(R)$
a	+4.72 176[−01]	−7.02 377[−02]
b	+6.82 857[−02]	+9.39 437[−02]
η	+1.19 489[+00]	+8.48 500[+00]
c_0	−6.63 570[−04]	−9.03 113[−05]
c_1	+2.73 115[−04]	+2.19 630[−05]
c_2	−2.77 551[−05]	−1.51 940[−06]
C_4	—	+1.83 924[−04]
C_6	−1.58 165[−02]	−3.63 613[−03]
C_8	−7.30 340[−01]	−3.76 238[−02]
C_{10}	−2.01 510[+02]	—

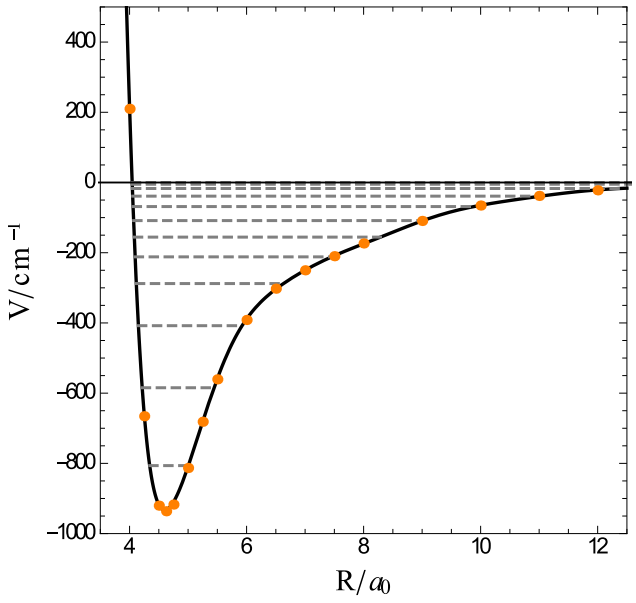

FIG. 2. Complete PEC for the $X^1\Sigma_g+$ state of Be_2 (solid black line); orange dots are the actual *ab initio* data points. The horizontal dashed lines are energies of the $J = 0$ vibrational levels. The horizontal black solid line denotes the onset of continuum.

IV. SPECTROSCOPIC DATA

The total PEC generated in this work was used to calculate the spectroscopic parameters of the ground state of the beryllium dimer. The well-depth (D_e) and the equilibrium bond length (R_e) are obtained by finding the minimum of the PEC numerically. This gives the values of $D_e = 933.3\,\mathrm{cm}^{-1}$ and $R_e = 2.4354\,\text{Å}$. We estimate that the error of the theoretically determined well-depth is at most $2.5\,\mathrm{cm}^{-1}$.

Let us compare these results with the experimental and theoretical data available in the literature. The original experimental result of Merritt *et al.* [34] is $D_e = 929.7\,\mathrm{cm}^{-1}$ employing the expanded Morse oscillator (EMO) model of the potential. This choice is not ideal for the beryllium dimer due to an unphysical decay at large interatomic distances. This deficiency was first pointed out by Patkowski *et al.* [36]. who employed "morphed" *ab initio* potential energy curves with the correct asymptotics. Depending on the number of parameters used in the morphing procedure the value of D_e varied in the range $933.0 - 934.6\,\mathrm{cm}^{-1}$, in almost perfect agreement with the present result. A similarly good agreement is found with the recent work of Meshkov *et al.* [37] where two empirical potentials have been determined by the direct-potential-fit procedure. The Morse-long range (MLR) and Chebyshev polynomial expansion (CPE) functions give $D_e = 934.8 \pm 0.3\,\mathrm{cm}^{-1}$ and $D_e = 935.0 \pm 0.3\,\mathrm{cm}^{-1}$, respectively. The most recent *ab initio* result of Koput [23], $D_e = 935 \pm 10\,\mathrm{cm}^{-1}$, is also well within the present error bars. In Table X we show a compilation of the spectroscopic data (D_e, R_e, D_0, etc.) obtained from selected experimental measurements, semi-empirical/morphed potentials, and pure *ab initio* calculations.

Let us note that in the recent theoretical work [24] we have predicted the well-depth to be $D_e = 929.0 \pm 1.9\,\mathrm{cm}^{-1}$. This is somewhat outside the error bars of the present work and *vice versa*. Because both results have been obtained with a very similar method this discrepancy requires a more detailed explanation. It turns out that most of the difference can be explained by the fact that the internuclear distance adopted in Ref. [24] does not correspond to the true minimum of the theoretical PEC. In Ref. [24] the calculations were performed only for a single value of R from the work of Merritt et al. [34]. If we evaluate the interaction energy at this point ($R_e = 2.4536\,\text{Å}$) by using PEC developed in this work we obtain $D_e = 931.8\,\mathrm{cm}^{-1}$ which is in a much better agreement with Ref. [24]. The slightly increased uncertainty of the present results comes mostly from the inaccuracy of the fit. We recommend that the present result ($D_e = 933.3 \pm 2.5\mathrm{cm}^{-1}$) is referenced in other works instead of the value given in Ref. [24].

Finally, we solve the (radial) nuclear Schrödinger equation with the help of the DVR method [83] to obtain the vibrational energy levels. The results are listed in Table XI and compared with the experimental results of Merritt et al. [34] We find a very good agreement between the theoretical and empirical vibrational energy terms. The average deviation is only about 0.8 cm^{-1} indicating that the spectroscopic accuracy has been indeed achieved. Additionally, note that the experimental uncertainty of the data of Ref. [34] is about 0.5 cm^{-1}, so that the actual accuracy of our *ab initio* results might be slightly better the average deviation suggests. Crucially, our PEC supports twelve vibrational levels confirming the prediction of Patkowski et al. [36] The last vibrational level calculated with the current PEC lies just 0.4 cm^{-1} away from the onset of the continuum. This is in a reasonably good agreement both with Refs. [36] where a value in the range 0.40−0.44 cm^{-1} was predicted, and with the most recent Ref. [37] where about 0.52 cm^{-1} was obtained. Despite our results favour the former value, the accuracy of PEC developed in this work is insufficient to give a definite answer.

V. CONCLUSIONS

The present work is a detailed first-principles theoretical study of the ground state of the beryllium dimer. An accurate *ab initio* potential energy curve for this system has been calculated with a composite scheme involving several quantum-chemical methods and large basis sets composed of Slater-type orbitals. The dominant (four-electron) valence contribution to the interaction energy has been calculated at the FCI level theory. The remaining inner-shell effects are treated with high-level coupled

TABLE X. Comparison of the selected empirical and theoretical results for the ground state of beryllium dimer. Energies are given in wavenumbers (cm^{-1}) and equilibrium distances in Ångströms (Å). The symbol $E_b(\nu = 11)$ denotes the binding energy of the last (twelfth) vibrational level. See the main text for definitions of other abbreviations.

Ref.	method	D_e	D_0	R_e	$E_b(\nu = 11)$
		empirical/morphed potentials			
[31]	ν extrapolation	790 ± 30	660	2.45	—
[34]	EMO	929.7 ± 2.0	806.53	2.4536	—
[33]	morphed 3-param.	922.9	795.0	2.4382	—
[36]	morphed 5-param.	934.6	807.4	2.438	0.42
[37]	MLR potential fit	934.8 ± 0.3	808.16	2.445	0.518
[37]	CPE potential fit	935.0 ± 0.3	808.20	2.445	0.521
		pure *ab initio* potentials			
[20]	CCSD(T)+FCI	944 ± 25	816	2.440	—
[25]	CAS r_{12}-MR-ACPF	898 ± 8	772	2.444	—
[21]	EXRHF	945 ± 15	819	2.452	—
[22]	CCSD(T)+FCI	938 ± 15	—	2.44	—
[23]	CCSD(T)+FCI	935 ± 10	808.3	2.444	0.4
this work	see the text	933.3 ± 2.5	806.4	2.4354	0.4

TABLE XI. Comparison of the vibrational energy terms for the $X^1\Sigma_g+$ state of the beryllium dimer ($J = 0$). The experimental values of Ref. [34] are listed in the second column, the *ab initio* values obtained in this work are listed in the third column, and the deviation is given in the last column. All values are given in wavenumbers (cm^{-1}).

ν	exp. [34]	this work	deviation
1	222.6	221.8	0.8
2	397.1	398.5	1.4
3	518.1	518.5	0.4
4	594.8	594.6	0.2
5	651.5	650.8	0.7
6	698.8	697.9	0.9
7	737.7	737.9	0.2
8	768.2	767.5	0.7
9	789.9	789.3	0.6
10	802.6	801.4	1.2
11	—	806.0	—

cluster methods such as CCSD(T) or CCSDT(Q).

To further increase the accuracy of our theoretical predictions we have perturbatively calculated corrections due to some small physical effects. This includes the relativistic corrections (full Breit-Pauli Hamiltonian) and the leading-order QED corrections. The finite nuclear mass effects (the non-Born-Oppenheimer effects) are found to be negligible at present.

Spectroscopic parameters generated by using the PEC developed in this work show a remarkably good agreement with the experimental data. This is true for the well-depth (calculated $D_e = 933.3 \pm 2.5 cm^{-1}$), binding energy ($D_0 = 806.4$), and the equilibrium bond length ($R_e = 2.4354$ Å). The vibrational energy terms are on average only 0.8 cm^{-1} away from the empirical results of Merritt et al. [34] showing that the spectroscopic accuracy has been achieved. We have confirmed the existence of the last (twelfth) vibrational state and predicted that it lies just 0.4 cm^{-1} below the onset of the continuum. Lastly, this study have proven that the Slater-type orbitals can routinely be used as a basis set for quantum-chemical calculations for diatomic systems.

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CHAPTER 4

Unpublished results

4.1. One-electron integrals with arbitrary interaction kernel

4.1.1. Form of one-electron operator

The first fundamental goal in quantum chemical *ab initio* calculations is to obtain accurate energies for the species under consideration. However, additional information about the system is required in many applications and the so-called molecular properties constitute an important class. Numerous properties are expressed as expectation values of one-electron operators (or combinations thereof). Therefore, in calculations employing a finite basis set the necessary step is to evaluate matrix elements of the operator of interest in this basis. Unfortunately, the number of properties (and thus operators) which are frequently considered is very large. Independent implementation of matrix elements for each operator is both time-consuming and error-prone. It would be more economical to devise a procedure general enough so that new operators can be implemented without a significant effort. This would lead to significant time savings, especially in the problematic steps of debugging and testing. In this section we present a general procedure to evaluate matrix elements of a broad class of one-electron operators in the basis of Slater-type orbitals.

Let us consider a diatomic molecule and introduce the following generic form a one-electron operator

$$\mathcal{V}(\mathbf{r}) = V(\mathbf{r}_a) + V(\mathbf{r}_b), \tag{4.1.1}$$

where

$$V(\mathbf{r}_a) = \sum_{lm}^{l_{\max}} f_{lm}(r_a) Y_{lm}(\hat{\mathbf{r}}_a), \tag{4.1.2}$$

and similarly for $V(\mathbf{r}_b)$. The procedure given below is valid both for a finite and an infinite $l_{\max}$. However, in the latter case the final expressions contain an infinite summation and have to be truncated for practical reasons. Unless stated otherwise, our intention is that $l_{\max} < \infty$.

The relevant matrix elements read

$$\mathcal{V}_{abc} = \int d\mathbf{r}\; r_a^{n_a-1} e^{-\zeta_a r_a}\, Y^*_{l_a m_a}(\hat{\mathbf{r}}_a)\, V(\mathbf{r}_b)\, r_c^{n_c-1} e^{-\zeta_c r_c}\, Y_{l_c m_c}(\hat{\mathbf{r}}_c). \tag{4.1.3}$$

For a diatomic molecule we encounter three unique classes of this general integral: $\mathcal{V}_{aaa}$, $\mathcal{V}_{baa}$, and $\mathcal{V}_{bab}$. The remaining cases can be obtained by invoking the permutational symmetry of the matrix elements $\mathcal{V}_{abc}$ and/or the $a \leftrightarrow b$ exchange symmetry.

Clearly, the formula (4.1.2) does not cover all possible operators one can come up with. For instance, it assumes separability in r_a and r_b. However, we believe that this stencil is reasonably broad and a myriad of well-known operators can be rewritten in this form. This includes, trivially, any scalar multiplicative operator, e.g. $r_a^n + r_b^n$ with $n > -3$. The electronic dipole moment operator, $\mathbf{r}_a + \mathbf{r}_b$, or the gradient of the potential operator, $\frac{\mathbf{r}_a}{r_a^3} + \frac{\mathbf{r}_b}{r_b^3}$ can easily be brought in the form (4.1.2) by including the appropriate terms with $l = 1$. Other examples will be given in the remainder of the text.

4.1.2. Matrix elements

The method we propose here is based on the spatial translation of STOs in the framework of the Barnett-Coulson method [150]

$$\begin{aligned}\frac{1}{\sqrt{\pi}}\, r_b^{n-1}\, e^{-\beta r_b}\, Y_{lm}(\theta_b,\phi_b) &= (-1)^{l-m}\left(2l+1\right)\sum_{\lambda=0}^{l}\frac{r_a^\lambda}{\sqrt{2\lambda+1}}\, Y_{\lambda m}(\theta_a,\phi_a)\,(-R)^{l-\lambda} \\ &\times \begin{pmatrix} \lambda & l-\lambda & \lambda \\ m & 0 & -m \end{pmatrix}\begin{pmatrix} 2l \\ 2\lambda \end{pmatrix}^{1/2}\sum_{k=0}^{\infty}\sqrt{2k+1}\, Y_{k0}(\theta_a,\phi_a)\,\zeta_{n-l,k}(\beta, r_a; R),\end{aligned} \tag{4.1.4}$$

where the function ζ_{nm} is formally defined through the integral representation

$$\zeta_{nm}(\beta, r_a; R) = \int_0^\pi d\theta_a\, \sin\theta_a\, P_m(\cos\theta_a)\, r_b^{n-1}\, e^{-\beta r_b}. \tag{4.1.5}$$

Further in the text we drop the parentheses from the definition of the ζ-function and write ζ_{nm} instead of $\zeta_{nm}(\beta, r_a; R)$ when it is clear from the context. The ζ_{nm}

function obeys a set of recursive relations

$$\zeta_{n+2,m} = \left(r_a^2 + R^2\right)\zeta_{nm} - \frac{2\,r_a\,R}{2m+1}\Big[m\,\zeta_{n,m-1} + (m+1)\,\zeta_{n,m+1}\Big], \tag{4.1.6}$$

and

$$\begin{aligned} \zeta_{1m} &= \frac{\beta\,r_a\,R}{2m+1}\Big[\zeta_{0,m-1} - \zeta_{0,m+1}\Big], \quad \text{for} \quad m > 0, \\ \zeta_{10} &= \beta\,r_a\,R\Big[\zeta_{00} - \zeta_{01}\Big] + e^{-\beta(r_a+R)}. \end{aligned} \tag{4.1.7}$$

Finally, to initiate the recursive process one requires

$$\zeta_{0m} = \frac{2\beta}{\pi}\,i_m(\beta\,r_<)\,k_m(\beta\,r_>), \tag{4.1.8}$$

where i_m and k_m are the modified spherical Bessel functions, $r_< = \min(r_a, R)$, and $r_> = \max(r_a, R)$. Additional comments on the Barnett-Coulson method are given in Paper V.

Let us begin with the atomic integrals, $\mathcal{V}_{aaa}$. By introducing the spherical coordinate system and integrating over the angles one gets

$$\begin{aligned} \mathcal{V}_{aaa} = \frac{(-1)^{m_a}}{2\sqrt{\pi}}\sqrt{(2l'_a+1)(2l_a+1)}\sum_{lm}^{l_{\max}}\begin{pmatrix} l_a & l & l_b \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} l_a & l & l_b \\ -m_a & m & m_b \end{pmatrix}\int_0^\infty dr_a\,r_a^{n_a+n'_a}\,e^{-(\zeta_a+\zeta'_a)r_a}\,f_{lm}(r_a) \end{aligned} \tag{4.1.9}$$

Obviously, the only remaining problem is the evaluation of the radial integral. We shall return to this issue once the two-centre integrals are solved.

In the two-centre case there are two unique integrals, $\mathcal{V}_{baa}$ and $\mathcal{V}_{bab}$. However, a product of two STOs located at the same point of space can always be written down as a linear combination of the individual STOs. As a result, the matrix element $\mathcal{V}_{bab}$ becomes just a special case of the most general integral, $\mathcal{V}_{baa}$. Thus, in the remainder of this section we concentrate solely on the latter quantity.

To handle the integral $\mathcal{V}_{baa}$ one returns to the definition (4.1.2) and notes that it contains two spherical harmonics located on the same centre. Therefore, by utilising

the standard relations for the coupling of two angular momenta

$$\mathcal{V}_{baa} = \sum_{lm}^{l_{\max}} \sqrt{\frac{(2l_a+1)(2l+1)}{4\pi}} \sum_{L=|l-l_a|}^{l+l_a} \sqrt{2L+1} \begin{pmatrix} l_a & L & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_a & L & l \\ m_a & M & m \end{pmatrix} \mathcal{V}^{ba}_{LM}, \tag{4.1.10}$$

where $M = -m_a - m$, and

$$\mathcal{V}^{ba}_{LM} = \int d\mathbf{r}\; r_b^{n_b-1} e^{-\zeta_b r_b}\, Y^*_{l_b m_b}(\hat{\mathbf{r}}_b)\, f_{lm}(r_a)\, r_a^{n_a-1} e^{-\zeta_a r_a}\, Y_{LM}(\hat{\mathbf{r}}_a). \tag{4.1.11}$$

The latter integral is solved by translating the orbital located at the centre b to the centre a. By inserting Eq. (4.1.4) and rearranging one obtains

$$\begin{aligned} \mathcal{V}^{ba}_{Lm_b} = (-1)^{l_b}\sqrt{2L+1}\,\frac{2l_b+1}{2} \sum_{\lambda=0}^{l_b} (-R)^{l_b-\lambda} \begin{pmatrix} \lambda & l_b-\lambda & \lambda \\ m_b & 0 & -m_b \end{pmatrix} \begin{pmatrix} 2l_b \\ 2\lambda \end{pmatrix}^{1/2} \\ \times \sum_{k=|\lambda-L|}^{k+L} (2k+1) \begin{pmatrix} \lambda & k & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \lambda & k & L \\ -m_b & 0 & m_b \end{pmatrix} W^{lm}_{\lambda+n_b+1,n_b-l_b,k}(\zeta_a,\zeta_b,R), \end{aligned} \tag{4.1.12}$$

where

$$W^{lm}_{ijk}\Big(a,b,R\Big) = \int_0^\infty dr\; r^i\, \zeta_{jk}\Big(b,r;R\Big)\, f_{lm}(r)\, e^{-ar}. \tag{4.1.13}$$

Note that the sum over k in Eq. (4.1.12) truncates by the virtue of the $3j$ coefficients (triangle inequality). Thus, there are no infinite summations in the final expressions. Further in the text we drop the parentheses from the definition of $W^{lm}_{ijk}\Big(a,b,R\Big)$, i.e. we write W^{lm}_{ijk} when the meaning is clear from the context. The remaining one-dimensional integrals (4.1.13) can be simplified by using the recursion relations (4.1.6) and (4.1.7) giving

$$W^{lm}_{i,j+2,k} = W^{lm}_{i+2,jk} + R^2\, W_{ijk} - \frac{2R}{2k+1}\Big[k\, W^{lm}_{i+1,j,k-1} + \Big(k+1\Big) W^{lm}_{i+1,j,k+1}\Big], \tag{4.1.14}$$

$$W^{lm}_{i1k} = \frac{bR}{2k+1}\Big[W^{lm}_{i+1,0,k-1} - W^{lm}_{i+1,0,k+1}\Big], \tag{4.1.15}$$

and

$$W_{i10}^{lm} = bR\left[W_{i+1,00}^{lm} - W_{i+1,01}^{lm}\right] + \frac{i!\, e^{-bR}}{(a+b)^{\,i+1}}. \tag{4.1.16}$$

To initiate the above recursions one needs the values of W_{i0k}^{lm}. By employing Eq. (4.1.8) we get

$$W_{i0k}^{lm} = \frac{2b}{\pi}\left[k_k\Big(bR\Big)\int_0^R dr\, r^i\, i_k(br)\, f_{lm}(r)\, e^{-ar} + i_k\Big(bR\Big)\int_R^\infty dr\, r^i\, k_k(br)\, f_{lm}(r)\, e^{-ar}\right]. \tag{4.1.17}$$

At this point the problem has been reduced to the calculation of two one-dimensional integrals. Together with the integral appearing in the atomic case [cf. Eq. (4.1.9)] we have three basic quantities

$$\begin{aligned} &\int_0^\infty dr\, r^i\, e^{-ar}\, f_{lm}(r), \\ &\int_0^R dr\, r^i\, i_k(br)\, f_{lm}(r)\, e^{-ar}, \\ &\int_R^\infty dr\, r^i\, k_k(br)\, f_{lm}(r)\, e^{-ar}. \end{aligned} \tag{4.1.18}$$

Our main goal in the present section is to make the procedure as general as possible. In other words, one should be able to perform calculations for different f_{lm} with very little changes to the code. Consequently, we propose to evaluate all three integrals (4.1.18) by numerical quadrature. We selected the Tanh-Sinh rule [462, 463] which is widely considered to be the most universal integration quadrature available at present [464, 465]. For the ordinary smooth functions this rule performs similarly as the usual Gaussian quadratures, but at the same time it is able to handle integrals with singularities, discontinuities, etc. In this way one can assure that the results of the calculations are reliable for a broad range of possible functions $f_{lm}(r)$. Further in the thesis we show some examples of important matrix elements where the procedure described above can be applied with minor or no changes. This illustrates usefulness of the proposed scheme.

4.2. Finite nuclear size models

4.2.1. Importance

In the Born-Oppenheimer approximation nuclei are assumed to have infinite mass and their positions are parameters of the electronic Schrödinger equation. Therefore, the nuclei are characterised solely by their charge distribution, $\rho_{\text{nuc}}(\mathbf{r})$, and generate some external potential, $V_{\text{nuc}}(\mathbf{r})$. These two quantities are related by the classical Poisson equation, $\nabla^2 V_{\text{nuc}}(\mathbf{r}) = -4\pi\rho_{\text{nuc}}(\mathbf{r})$ in the atomic units. Additionally, the charge distribution is subject to a normalisation condition, $\int d\mathbf{r}\, \rho_{\text{nuc}}(\mathbf{r}) = Z$, where Z is the nuclear charge.

The most common approximation for the nuclear charge distribution is the point-like source, i.e. $\rho_{\text{nuc}}(\mathbf{r}) = Z\delta(\mathbf{r})$. This charge distribution generates the usual Coulomb potential, $V_{\text{nuc}}(\mathbf{r}) = -Z/r$. This approach is sufficient for most elements of the periodic table and thus implemented by default in all general quantum chemistry packages. From now on, we assume that the nuclear charge distributions are spherically symmetric, i.e. instead of $\rho_{\text{nuc}}(\mathbf{r})$ we simply write $\rho_{\text{nuc}}(r)$ in all subsequent formulae. The same simplification is adopted for the corresponding nuclear potentials.

There are two main reasons to adopt a different model for the nuclear charge distribution in quantum chemical calculations. First, the classical Coulomb model becomes insufficient for heavy nuclei and leads to inaccurate results [466]. Second, by adopting a more smooth (i.e. nonsingular at the origin) nuclear potential one avoids problems with the nuclear cusp condition [467]. In this way, basis set requirements can be considerably reduced; this is potentially important for all elements.

The exact theoretical description of the nuclei is given, in principle, by the quantum chromodynamics (QCD). By solving QCD equations one could theoretically obtain the exact residual potential generated by a system of interacting quarks and use it in subsequent description of the electrons. Unfortunately, this approach is abysmally difficult (and unfeasible in practice) due to very complicated nature of the interactions between many quarks comprising the nuclei. Therefore, one is forced to use some nuclear models which are largely arbitrary and require some reference to empirical data.

Here, we consider three popular nuclear models and show how they can be incorporated into quantum chemical calculations within the STOs basis set. In every model the so-called root-mean-square radius (RMS) of the nucleus is used, $\langle R^2 \rangle$.

It is given by an approximate formula, $\sqrt{\langle R^2 \rangle} = 0.836A^{1/3} + 0.570$ fm, where A is the mass number [468]. This approximation was obtained by fitting the experimental values and is accurate to within 0.05 fm for all elements. We prefer to use this formula instead of the actual empirical data because of simplifications in the implementation. Moreover, no data have to be supplied by the user.

4.2.2. Popular approaches

The first important nuclear model is the homogeneously charged sphere (HCS) [469–472]. As the name suggests it assumes that the charge of the nucleus is evenly distributed on a sphere with radius R_0. The radius R_0 is related to $\langle R^2 \rangle$ by means of the formula $R_0 = \sqrt{\frac{5}{3}\langle R^2 \rangle}$. One can show that the exact expression for the potential in this model reads [473]

$$V_{\mathrm{HCS}}(r) = -\frac{Z}{2R_0}\left(3 - \frac{r^2}{R_0^2}\right), \quad \text{for } r \leqslant R_0, \tag{4.2.1}$$

$$V_{\mathrm{HCS}}(r) = -\frac{Z}{r}, \quad \text{for } r > R_0. \tag{4.2.2}$$

Next, we consider the Gaussian nuclear model assuming that the nuclear charge is given by a single Gaussian function, $\rho_G(r) = Z\left(\frac{\xi}{\pi}\right)^{3/2} e^{-\xi r^2}$. The related potential is given by a simple formula [474]

$$V_{\mathrm{G}}(r) = -\frac{Z}{r}\mathrm{erf}\left(\sqrt{\xi} r\right), \tag{4.2.3}$$

where erf is the error function and $\xi = \frac{3}{2\langle R^2 \rangle}$. Of course, instead of a single Gaussian function one could use a linear combination of Gaussians to obtain a more reliable model. However, this introduces more parameters into the equations. These parameters are no longer given by any simple expression but must be obtained by a brute-force fitting of the experimental data. Therefore, this scheme is not implemented in our program.

Finally, we consider the most "physical" model of the nucleus - the Fermi 2-parameter charge distribution [468]. It is given by a formula

$$\rho_F(r) = \frac{\rho_0}{1 + e^{4\ln 3(r-c)/t}}, \tag{4.2.4}$$

where the parameters c and t are the half charge radius and the skin thickness, respectively. Heuristically, c is the value of r at which the nuclear charge distribution

falls to half of its value at $r = 0$, i.e. $\rho_F(c) = \frac{1}{2}\rho_0$, and t is the length of the interval in which $\rho_F(r)$ falls from $\frac{9}{10}\rho_0$ to $\frac{1}{10}\rho_0$. The value of ρ_0 is fixed by the aforementioned normalisation condition. It is also common to assume that $t = 2.30$ fm for all nuclei. The expression for c is [466]

$$c = \sqrt{R_0^2 - \frac{7}{3}\left(\frac{\pi t}{4\ln 3}\right)^2}, \tag{4.2.5}$$

for $A > 5$ and

$$c = 2.2291 \cdot 10^{-5} a_0 \, A^{1/3} - 0.90676 \cdot 10^{-5} a_0, \tag{4.2.6}$$

for lighter nuclei, where a_0 is the Bohr radius. The latter formula was obtained by fitting to the experimental data. The potential in the Fermi model is not given by any closed-form analytic formula. However, because the value of c is very small the following series expansions are sufficient [475]

$$\begin{aligned} -rV_{\mathrm{F}}(r) = \frac{Z}{N}\Bigg\{ & 6\left(\frac{a}{c}\right)^3 \left[S_3\left(\frac{r-c}{a}\right) - S_3\left(-\frac{c}{a}\right)\right] - \frac{1}{2}\left(\frac{r}{c}\right)^3, \\ & + \frac{r}{c}\left[\frac{3}{2} + \frac{1}{2}\pi^2\left(\frac{a}{c}\right)^2 - 3\left(\frac{a}{c}\right)^2 S_2\left(\frac{r-c}{a}\right)\right]\Bigg\}, \qquad \text{for } r \leqslant c, \\ -rV_{\mathrm{F}}(r) = \frac{Z}{N}\Bigg\{ & N + 3\left(\frac{a}{c}\right)^2 \left[\frac{r}{c} S_2\left(\frac{c-r}{a}\right) + \frac{2a}{c} S_3\left(\frac{c-r}{a}\right)\right]\Bigg\}, \qquad \text{for } r > c, \end{aligned} \tag{4.2.7}$$

where $a = t/4\ln 3$, and the normalisation constant is $N = 1 + \pi^2\left(\frac{a}{c}\right)^2 - 6\left(\frac{a}{c}\right)^3 S_3\left(-\frac{c}{a}\right)$. Both expansions converge to the machine precision after just several terms and thus do not introduce any additional error to the final results. The special function S_k is defined through the formula [475]

$$S_k(z) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n^k} e^{nz}, \tag{4.2.8}$$

for $z < 0$. We found that under the conditions defined by Eqs. (4.2.7) this series converges rapidly for all required z. Parenthetically, S_k can alternatively be expressed through the well-known polylogarithm function, Li_n.

Clearly, calculations of the two-centre STOs matrix elements with the potentials

defined by Eqs. (4.2.1), (4.2.3) or (4.2.7) would be very difficult if approached with fully analytic techniques. In particular, each nuclear model would probably require a separate treatment and many hundreds (if not thousands) of lines of code. However, if we employ the general scheme described in the previous section we only need to evaluate three radial integrals (4.1.18) with f_{00}. Numerical evaluation of these integrals is relatively straightforward since the calculation of the nuclear potentials themselves can easily be implemented in several lines of code each. As a result, three models of the nuclei described above are implemented in our program in a completely general fashion. The accuracy is decent in a wide range of A. The user has to choose the nuclear model with a proper keyword and then select the mass number A. The program automatically evaluates all necessary parameters (R_0, ξ, c, t, etc.) by using the proper formulae and then passes to the evaluation of the matrix elements. Therefore, from the point of view of the user, calculations with one of the three finite nuclear size potentials are as straightforward as with the ordinary Coulomb potential. In particular, no additional empirical data must be provided.

4.3. Integrals for explicitly correlated theories

4.3.1. Importance

As mentioned in the introduction, a considerable majority of the electronic structure methods represent the trial electronic wavefunction as a linear combination of the Slater determinants. This approach is general and elegant but leads to a relatively slow convergence of the energy (and other properties) with respect to the size of the basis set. The reason for this problematic behaviour is now well-understood and related to the analytic structure of exact electronic wavefunction, i.e. the cusp condition (1.3.2) at the collision points of two electrons. This condition is impossible to satisfy exactly with any expansion in products of one-electron functions. Hill [476] and other authors [477–480] demonstrated that this leads to the L^{-3} error decay in the conventional energy calculations (L is the largest angular momentum present in the basis set).

The most natural way to circumvent this problem is to include the interelectronic distance directly into the trial wavefunction, i.e. abandon the algebraic approximation. The first realisations of this idea were presented by Byron and Joachain [484], Pan and King [485, 486], Szalewicz and co-workers [487–491], and later by Adamowicz and Sadlej [492–494]. The methods developed by these authors were based

mostly on the explicitly correlated Gaussian (ECG) functions. Despite being able to provide high accuracy they require extensive nonlinear optimisations and are thus limited to small systems. A revolution came with the works of Kutzelnigg and collaborators [479, 495–500]. They introduced a class of R12/F12 methods where the dependence on r_{12} is introduced by multiplying products of occupied Hartree-Fock orbitals by the so-called correlation factor, f_{12}. This is a universal function dependent solely on r_{12}. In the early approaches the simple choice $f_{12} := r_{12}$ was adopted (R12 methods), but the theory was later extended to allow for an arbitary mathematical form of f_{12} (F12 methods) [481–483]. Since then the general idea of R12/F12 has been progressively refined and improved by various authors (see Refs. [501, 502] for a recent review). Today, explicitly correlated theories can be used for molecules with hundreds of electrons to reach chemical accuracy with small basis sets as well as for small systems to provide (sub-)spectroscopic accuracy [501, 502]. Notably, in the F12 methods the energy converges to the basis set limit as L^{-5} or L^{-7}, depending on the type of approximations used in the calculations. This is a considerable improvement over the conventional L^{-3} error decay.

4.3.2. Types of integrals

Because of the undeniable advantages of the explicitly correlated methods, it is an obvious question whether Slater-type orbitals can be used as a basis set in F12 calculations. The answer depends critically on the mathematical form of f_{12} which is supposed to be used. Nowadays, the most successful proposal for f_{12} is the exponential formula introduced by Ten-no [503, 483], $f(r_{12}) := e^{-\gamma r_{12}}$. Other formulae were also proposed, but are significantly more complicated [504] or only marginally more effective [505]. Unfortunately, the task of combining the exponential formula for f_{12} with STOs is rather daunting. This is mostly due to complicated nature of various matrix elements which are necessary to perform the F12 calculations. It is now a well-established fact [504, 506, 507] that in the F12 theories the following types of two-electron integrals appear

$$(ab|\hat{\mathcal{K}}|cd) = \iint d\mathbf{r}_1\, d\mathbf{r}_2\; \varphi_a^*(\mathbf{r}_1)\, \varphi_c^*(\mathbf{r}_2)\, \hat{\mathcal{K}}\, \varphi_b(\mathbf{r}_1)\, \varphi_d(\mathbf{r}_2), \tag{4.3.1}$$

where the operator $\hat{\mathcal{K}}$ is any of the following

$$r_{12}^{-1},\; r_{12}^{-1} f_{12},\; f_{12},\; f_{12}^2,\; \left[f_{12}, \hat{t}_1\right],\; \left[f_{12}, \left[f_{12}, \hat{t}_1\right]\right], \tag{4.3.2}$$

with $\hat{t}_n = -\frac{1}{2}\nabla_n^2$. Let us first perform a few manipulations in the above expressions to reveal the true basic quantities. The first four integrals must be computed as they stand. The fifth integral can be simplified by noting that

$$\Big[f_{12}, \hat{t}_1\Big] = \frac{1}{2}\Big(\nabla_1^2 f_{12}\Big) + \Big(\nabla_1 f_{12}\Big)\cdot\nabla_1, \tag{4.3.3}$$

and making use of the second Green's identity. This leads to

$$\begin{aligned}&(ab|\Big[f_{12}, \hat{t}_1\Big]|cd) = \\ &\frac{1}{2}\iint d\mathbf{r}_1\, d\mathbf{r}_2 \left[\Big[\nabla_1^2\varphi_a^*(\mathbf{r}_1)\Big]\,\varphi_b(\mathbf{r}_1) - \varphi_a^*(\mathbf{r}_1)\,\Big[\nabla_1^2\varphi_b(\mathbf{r}_1)\Big]\right] f_{12}\,\varphi_c^*(\mathbf{r}_2)\,\varphi_d(\mathbf{r}_2).\end{aligned} \tag{4.3.4}$$

Because of the obvious identity

$$\nabla^2\Big[r^{n-1}e^{-\zeta r}\,Y_{lm}(\theta,\phi)\Big] = \Big[\Big[n(n-1) - l(l+1)\Big]r^{n-3} - 2\,n\,\zeta\,r^{n-2} + \zeta^2 r^{n-1}\Big]Y_{lm}(\theta,\phi)\,e^{-\zeta r},$$

the integrals $(ab|\Big[f_{12}, \hat{t}_1\Big]|cd)$ are fundamentally of the same type as $(ab|f_{12}|cd)$. There is an additional inconvenience connected with the fact that the power of r is reduced after the action of the Laplacian. Calculation of two-electron integrals with such functions (non-canonical Slater-type orbitals) is considered further in the thesis. Moreover, the integrals $(ab|\Big[f_{12}, \hat{t}_1\Big]|cd)$ have a smaller number of symmetries than the typical electron repulsion integrals. Instead of the usual eightfold symmetry we have the following relations

$$(ab|\Big[f_{12}, \hat{t}_1\Big]|cd) = (ab|\Big[f_{12}, \hat{t}_1\Big]|dc) = -(ba|\Big[f_{12}, \hat{t}_1\Big]|cd) = -(ab|\Big[f_{12}, \hat{t}_1\Big]|dc), \tag{4.3.5}$$

and there is no symmetry related to the exchange of the electrons, i.e. $(ab|\Big[f_{12}, \hat{t}_1\Big]|cd) \neq (cd|\Big[f_{12}, \hat{t}_1\Big]|ab)$. This reduced number of symmetries is somewhat challenging, e.g. the standard codes cannot be used for four-index transformations and other manipulations.

Finally, let us consider the last integral. The following expression is straightforward to derive if one takes into account that f_{12} is dependent only on the interelectronic distance

$$\Big[f_{12}, \Big[f_{12}, \hat{t}_1\Big]\Big] = \left(\frac{\partial f_{12}}{\partial r_{12}}\right)^2. \tag{4.3.6}$$

This expression can be used as it stands and the sixth integral becomes analogous

to the third and the fourth.

Let us now discuss the optimal choice of f_{12} for explicitly correlated calculations with Slater-type orbitals. The correlation factor of Ten-no [$f(r_{12}) = e^{-\gamma r_{12}}$] leads to two-electron integrals with the Yukawa potential and its derivatives. To the best of our knowledge, two general methods exist in the literature for evaluation of these integrals. The first is based on the solution of the Helmholtz equation ($\nabla^2 f + k^2 f = 0$) by the method of separation of variables in prolate spheroidal coordinates. This is a direct counterpart of the Neumann expansion for r_{12}^{-1}. Unfortunately, the former expansion is much more complicated and involves the so-called spheroidal wavefunctions [508] for which no closed-form expressions exist (in contrast to the Legendre functions found in the Neumann expansion). Therefore, the integrals with the Yukawa potential require a doubly infinite expansion to be evaluated in the ellipsoidal coordinates (or additional troublesome numerical integrations). This is clearly by an order of magnitude more difficult than any of the integrals considered in this thesis.

The second method for the evaluation of the integrals with the Yukawa potential is based on the so-called integration-by-parts identities. This method has been developed by the present author [335] and independently by Pachucki [336]. The most appealing aspect of this method is the fact that it involves only closed-form recursion relations and a single well-behaved numerical integration. Therefore, any infinite summations are entirely avoided. However, this comes at a cost of very complicated, multidimensional recursion relations and calculation of myriads of auxiliary functions. Moreover, most of the recursions contain apparent singularities and no general methods seem to exist to remove them from appearing in the calculations. Lastly, some of the relations involve serious numerical instabilities and require extended arithmetic precision to give reliable results. We believe that an ingenious reformulation of this theory is necessary to make it practical and efficient enough to be applied for systems larger than two electrons.

All the aforementioned problems force us to deviate from the notion of the exponential correlation factor. Fortunately, other reasonable proposals for the mathematical form of f_{12} can be put forward. This includes a simple third-order polynomial formula alike

$$f_{12} = r_{12}\left(1 + c_3 r_{12}^2\right). \tag{4.3.7}$$

Note that even powers of r_{12} have been removed from the above expression. In fact,

r_{12}^{2n} are expressible through products of one-electron functions, so that their inclusion would lead to an unwanted overlap with the conventional orbital expansion and increase the number of free parameters unnecessarily. The choice of the correlation factor given by Eq. (4.3.7) has several important merits. First, it contains no nonlinear parameters which simplifies the optimisation. Second, it is simple to prove that all fundamental integrals (4.3.1) can be assembled from only two classes of matrix elements

$$(ab|r_{12}^n|cd) \quad \text{and} \quad (ab|\left[r_{12}^n, \hat{t}_1\right]|cd), \tag{4.3.8}$$

where $n \geqslant -1$ in the first integral and $n \geqslant 1$ in the second one. Let us also point out that the above matrix elements are independent of the free parameters present in Eq. (4.3.7). This would be true even if the formula (4.3.7) included a larger number of powers of r_{12}. Therefore, if the corresponding computer program is cleverly written, the optimisation of the parameters can be performed in a single step without an expensive recalculation of all necessary integrals.

4.3.3. Evaluation

In this section we consider the evaluation of the matrix elements (4.3.8) necessary for explicitly correlated calculations with the correlation factor in the form (4.3.7) within the basis set of Slater-type orbitals. We concentrate solely on a method to evaluate the integral $(ab|r_{12}^n|cd)$. Calculation of the second matrix element is a relatively simple extension if one takes into account the theory presented in the next sections.

The methodology of calculation of $(ab|r_{12}^n|cd)$ depends substantially on the location of the orbitals, i.e. whether the orbitals under the integral sign are located on the centre a or b of a diatomic molecule. Following Papers I and II we distinguish the atomic $(aa|aa)$, Coulomb $(aa|bb)$, hybrid $(ab|bb)$, and exchange $(ab|ab)$ cases. As detailed in the Paper I, the first step in the calculations of the atomic, Coulomb and hybrid electron repulsion integrals is the Laplace expansion of r_{12}^{-1}. To provide a natural extension of this method to the integrals $(ab|r_{12}^n|cd)$ one requires an analogue of the Laplace expansion for r_{12}^n with $n \geqslant -1$. It turns out that this theoretical tool has already been used by some authors. We follow a particularly elegant approach

due to Sack [509] who derived the following formula

$$r_{12}^{n} = \sum_{L=0}^{L_{\max}} \frac{4\pi}{2L+1} \sum_{k=0}^{k_{\max}} C_{nLk}\, r_{>}^{n} \left(\frac{r_{<}}{r_{>}}\right)^{L+2k} \sum_{M=-L}^{L} Y_{LM}^{*}(\theta_1,\phi_1)\, Y_{LM}(\theta_2,\phi_2), \tag{4.3.9}$$

where $r_{<} = \min(r_1, r_2)$, $r_{>} = \max(r_1, r_2)$, and

$$L_{\max} = \infty, \quad k_{\max} = \frac{1}{2}(n+1) \quad \text{for odd } n, \tag{4.3.10}$$

$$L_{\max} = \frac{1}{2}n, \quad k_{\max} = \frac{1}{2}n - L \quad \text{for even } n. \tag{4.3.11}$$

One can see that the expansion is finite for even n. The numerical coefficients are given by the formula

$$C_{nLk} = \frac{2L+1}{n+2}\binom{n+2}{2k+1} \sum_{i=0}^{\min[L-1,\frac{1}{2}(n+1)]} \frac{2k+2i-n}{2k+2L-2i+1}. \tag{4.3.12}$$

This expansion was used numerous times in the calculations of the atomic many-electron integrals (see, for example, Ref. [510]). The biggest advantage of Eq. (4.3.9) is related to its universal character. It is valid both for even and odd n, includes the Laplace expansion as a special case and can easily be extended even to the very demanding $n = -2$ case. Therefore, it is particularly useful from the computational point of view.

Let us now derive the counterpart of Eq. (17) from Paper I valid for r_{12}^{n}. After inserting Eq. (4.3.9) and elementary rearrangements one obtains

$$\begin{aligned} &\int d\mathbf{r}_2\, r_{12}^{n}\, r_{2b}^{n_{34}-2}\, Y_{L_2M}(\cos\theta_{2b},\phi)\, e^{-\zeta_{34} r_{2b}} = \frac{4\pi}{2L_2+1} \frac{Y_{L_2M}(\cos\theta_{1b},\phi)}{\zeta_{34}^{n+n_{34}+1}} \\ &\times \sum_{k=0}^{k_{\max}} C_{nLk} \Big[(\zeta_{34} r_{1b})^{n_{34}+n+1}\, a_{n+n_{34}+L_2+2k}(\zeta_{34} r_{1b}) \\ &+ (n+n_{34}-L_2-2k)!\, e^{-\zeta_{34} r_{1b}} \sum_{j=L_2+2k}^{n+n_{34}} \frac{(\zeta_{34}\, r_{1b})^{j}}{(j-L_2-2k)!} \Big]. \end{aligned} \tag{4.3.13}$$

One can easily verify that by setting $n = -1$ and noting that $C_{-1,L_2,0} = 1$ the original equation (17) from the Paper I is recovered. Next, the expression (4.3.13) can be inserted into Eqs. (15) and (16) of Paper I. For the Coulomb integrals this

gives

$$\widetilde{I}_C = \frac{4\pi}{2L_2+1}\frac{1}{\zeta_{34}^{n_{34}+n+1}}\sum_{k=0}^{k_{\max}} C_{nLk}\Big[\zeta_{34}^{n_{34}+n+1}\int d\mathbf{r}_1\, r_{1a}^{n_{12}-2}\, Y_{L_1M}(\cos\theta_{1a},\phi)\, e^{-\zeta_{12}r_{1a}}$$
$$r_{1b}^{n_{34}+n+1}\, Y_{L_2M}(\cos\theta_{1b},\phi)\, a_{n_{34}+L_2+2k}(\zeta_{34}r_{1b}) + (n+n_{34}-L_2-2k)!\sum_{j=L_2+2k}^{n_{34}+n}\frac{\zeta_{34}^j}{(j-L_2-2k)!}$$
$$\times\int d\mathbf{r}_1\, r_{1a}^{n_{12}-2}\, Y_{L_1M}(\cos\theta_{1a},\phi)\, e^{-\zeta_{12}r_{1a}}\, r_{1b}^j\, Y_{L_2M}(\cos\theta_{1b},\phi)\, e^{-\zeta_{34}r_{1b}}\Big], \tag{4.3.14}$$

with a very similar expression for $\widetilde{I}_H$. Clearly, no new basic integrals appear and all necessary quantities can be calculated with the same methods as introduced in Paper I. The only difference is the additional summation over k and increased values of some parameters. For completeness, let us also give the expression for the atomic integrals with r_{12}^n which reads

$$\begin{aligned}\widetilde{I}_A = (-1)^{m_1+m_3}&\sqrt{\prod_{i=1}^{4}(2l_i+1)}\sum_L\begin{pmatrix} l_1 & L & l_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_3 & L & l_4\\ 0 & 0 & 0\end{pmatrix}\sum_{k=0}^{k_{\max}} C_{nLk}\\ &\times\Big[I^{>}_{L+2k}(n_{12},n_{34}+n+1;\zeta_{12},\zeta_{34}) + I^{<}_{L+2k}(n_{12}+n+1,n_{34};\zeta_{34},\zeta_{12})\Big]\\ &\times\sum_{M=-L}^{L}(-1)^M\begin{pmatrix} l_1 & L & l_2\\ -m_1 & -M & m_2\end{pmatrix}\begin{pmatrix} l_3 & L & l_4\\ -m_3 & M & m_4\end{pmatrix}.\end{aligned} \tag{4.3.15}$$

We skip the detailed derivation here and note only that the final formula can be obtained by the same technique as in the Supplementary Material to Paper I and with the help of Eq. (4.3.13).

Let us now turn our attention to the exchange integrals, $(ab|ab)$. We would like to extend the method pursued in Paper II (based on the Neumann expansion of r_{12}^{-1}) to include factors like r_{12}^n. A natural question is whether an analogue of the Neumann expansion for higher powers of the interelectronic distance exists. The answer is affirmative - this problem has been considered by Budziński and Prajsnar [242, 243] who introduced two equivalent expansions. The first is a straightforward generalisation of the Neumann expansion and the second is a more subtle approach based on polynomials orthogonal on $[1,\infty)$. Unfortunately, both of these methods are quite complicated and we did not manage to implement them in the most general way. Instead, we prefer to treat each power of r_{12} separately.

First, let us point out that even powers of r_{12} are not problematic. They can

be straightforwardly rewritten as combinations of dipole, quadruple etc. moment integrals by noting that $r_{12}^2 = x_1^2 - 2x_1x_2 + x_2^2 + \ldots$. Therefore, the integrals with even powers of r_{12} are assembled from much simpler one-electron integrals without any need for an expansion in ellipsoidal coordinates.

The odd powers of r_{12} are much more complicated. By recalling the definition of the prolate spheroidal coordinate system one can derive the following expression

$$\begin{aligned} r_{12}^2 = \left(\frac{R}{2}\right)^2 \Big[& \xi_1^2 + \xi_2^2 + \eta_1^2 + \eta_2^2 - 2 - 2\,\xi_1\,\xi_2\,\eta_1\,\eta_2 \\ & - \Big[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)\Big]^{1/2} \Big[e^{i(\phi_1-\phi_2)} + e^{-i(\phi_1-\phi_2)}\Big] \Big]. \end{aligned} \tag{4.3.16}$$

Let us take the first power of r_{12} as an example. The analytic formula for $(ab|r_{12}|a'b')$ is obtained by combining the obvious expression $r_{12} = r_{12}^{-1} \cdot r_{12}^2$ with Eqs. (2) and (3) from Paper II. Because the final expression is quite lengthy we give it in the Appendix A.

One can see that the formula for $(ab|r_{12}|a'b')$ is already quite cumbersome. We derived similar expressions for the integrals involving r_{12}^3 and r_{12}^5. While the explicit formula for the former involves a couple dozens of terms and is still rather manageable, the number of terms necessary for the integrals with r_{12}^5 goes into hundreds and cannot be implemented by hand. This is also why we are sceptical about the practical application of the general theory of Budziński and Prajsnar [242, 243]. Even if the formulae for r_{12}^{2n} could be implemented in a universal fashion, the number of terms in the working expressions would probably be very large making the resulting algorithm too costly and inefficient to be used in practice.

Let us note that if we restrict ourselves to the correlation factor (4.3.7) involving (at most) the third power of the interelectronic distance, the integrals with powers higher than r_{12}^6 are unnecessary. The correlation factor (4.3.7) is certainly sufficient to reduce the error of the calculations to a few microhartrees per electron pair - an accuracy sufficient for a majority of practical purposes. Moreover, if we further simplify the theory and set $f_{12} = r_{12}$ then only integrals with r_{12} and r_{12}^2 are necessary. Both are relatively simple to implement.

4.4. Atomic integrals with any interelectronic interaction

4.4.1. Justification

In this section we would like to consider calculation of the atomic integrals with arbitrary interaction between the particles. They take the following general form

$$(ab|\hat{\mathcal{K}}|cd) = \iint d\mathbf{r}_1\, d\mathbf{r}_2\; \varphi_a^*(\mathbf{r}_1)\, \varphi_b(\mathbf{r}_1)\, \hat{\mathcal{K}}(r_{12})\, \varphi_c^*(\mathbf{r}_2)\, \varphi_d(\mathbf{r}_2). \tag{4.4.1}$$

We do not impose any particular form of the interaction $\hat{\mathcal{K}}$ at this point. We assume only that $\hat{\mathcal{K}}$ is a scalar function of r_{12} and that it is sufficiently well-behaved to assure the existence of the integrals (4.4.1) in the usual sense. The reason for considering such integrals may not be immediately obvious - after all, the present thesis is devoted mostly to the diatomic systems. Therefore, we believe that some explanation and justification is necessary.

Our interest in the integrals (4.4.1) was sparked by the recent paper devoted to the asymptotic form of the correlation factor in explicitly correlated calculations [504]. It has been shown analytically how f_{12} behaves for large interelectronic distances. Because the short-range form of f_{12} is determined by the Kato's cusp condition, a new functional form of f_{12} has been proposed which interpolates smoothly between the short- and long-range regimes (the range-separated formula). It is worth noticing that the main results of Ref. [504] were obtained for the helium atom as a model system. While we believe that the new form of f_{12} is equally well-applicable to molecules, many-electron atoms constitute a natural proving ground. Notably, precision calculations both for few- and many-electron atoms are still in high demand [511–513]. As detailed in the previous sections, several new two-electron integrals are necessary to perform explicitly correlated calculations for many-electron systems. Most of them take the form (4.4.1) and constitute the biggest obstacle in pioneering applications of the range-separated correlation factor. However, this is not the only reason for our interest in the integrals (4.4.1). They are also necessary for first-principles simulations of the ultracold fermionic gases with realistic interatomic potentials. This is an active area of research nowadays [514].

4.4.2. Treatment

Because all orbitals under the integral sign in Eq. (4.4.1) occupy the same position in space, the first simplification is to expand both products of two Slater-type orbitals into linear combinations of STOs. This can be done with standard algebra

of the angular momentum without introducing any approximations. The integrals (4.4.1) reduce to linear combinations of the following quantities

$$\begin{aligned}&(L_1M|\hat{\mathcal{K}}|L_2M) = \\ &\iint d\mathbf{r}_1\, d\mathbf{r}_2\, r_1^{I-1}\, r_2^{J-1}\, e^{-\alpha r_1-\beta r_2}\, Y^*_{L_1M}(\theta_1,\phi_1)\, Y_{L_2M}(\theta_2,\phi_2)\, \hat{\mathcal{K}}(r_{12}).\end{aligned} \tag{4.4.2}$$

An important step here is to realise that the above integrals are independent of M. This conclusion follows easily from the Wigner-Eckart theorem in the case of a scalar function $\hat{\mathcal{K}}(r_{12})$ [see, for example, Ref. [515], Eqs. (6.3-1a) and (6.3-1b)]. Additionally, the integrals are non-zero if and only if $L_1 = L_2$. Therefore, we can sum over all M on the right-hand-side of Eq. (4.4.2) and divide by $2L+1$

$$\begin{aligned}(LM|\hat{\mathcal{K}}|LM) = &\iint d\mathbf{r}_1\, d\mathbf{r}_2\, r_1^{I-1}\, r_2^{J-1}\, e^{-\alpha r_1-\beta r_2}\, \hat{\mathcal{K}}(r_{12}) \\ &\times\frac{1}{2L+1}\sum_{M=-L}^{L} Y^*_{LM}(\theta_1,\phi_1)\, Y^*_{LM}(\theta_2,\phi_2).\end{aligned} \tag{4.4.3}$$

The sum under the integral sign in the above expression can be further simplified by using the spherical harmonics addition theorem [see, for example, Ref. [515], Eq. (1.2-21)]. This brings us to

$$(LM|\hat{\mathcal{K}}|LM) = \frac{1}{4\pi}\iint d\mathbf{r}_1\, d\mathbf{r}_2\, r_1^{I-1}\, r_2^{J-1}\, e^{-\alpha r_1-\beta r_2}\, \hat{\mathcal{K}}(r_{12})\, P_L(\cos\theta_{12}), \tag{4.4.4}$$

where P_L are the Legendre polynomials and $\cos\theta_{12}$ is the angle between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. Let us now change the variables of the integration. The integral can be transformed from the initial Cartesian coordinates to the new coordinates

$$\xi = \frac{r_1+r_2}{r_{12}} \quad \eta = \frac{r_1-r_2}{r_{12}}, \quad \text{and} \quad r_{12}, \tag{4.4.5}$$

and three Euler angles. The integrand does not depend on the angles, so they can be integrated out straightforwardly giving $8\pi^2$. This leads to

$$\begin{aligned}(LM|\hat{\mathcal{K}}|LM) = 2^{-I-J}\pi &\int_0^\infty dr_{12}\, r_{12}^{I+J+3}\, \hat{\mathcal{K}}(r_{12}) \int_1^\infty d\xi \int_{-1}^{+1} d\eta\, P_L(\cos\theta_{12}) \\ &\times (\xi+\eta)^I(\xi-\eta)^J\, e^{-\alpha\, r_{12}\,\xi}\, e^{-\beta\, r_{12}\,\eta},\end{aligned} \tag{4.4.6}$$

where the analogy with the ellipsoidal coordinate system is obvious. The next step is to get rid of the Legendre polynomial. The following closed-form expression for

P_L is useful here

$$P_L(\cos\theta_{12}) = 2^{-L}\sum_{k=0}^{L}\binom{L}{k}^2(\cos\theta_{12}-1)^{L-k}\,(\cos\theta_{12}+1)^k\,, \tag{4.4.7}$$

which can easily be obtained by solving the Bonnet's recursion formula [516]. If the terms including the cosine of the angles are transformed to the new coordinates with the help of elementary relationships

$$\cos\theta_{12}-1 = 2\,\frac{(\eta+1)(\eta-1)}{(\xi-\eta)(\xi+\eta)}, \tag{4.4.8}$$

$$\cos\theta_{12}+1 = 2\,\frac{(\xi+1)(\xi-1)}{(\xi-\eta)(\xi+\eta)}, \tag{4.4.9}$$

one arrives at

$$\begin{aligned}(LM|\hat{\mathcal{K}}|LM) = 2^{-I-J}\pi\sum_{k=0}^{L}\binom{L}{k}^2\int_0^\infty dr_{12}\,r_{12}^{I+J+3}\,\hat{\mathcal{K}}(r_{12})\int_1^\infty d\xi\int_{-1}^{+1}d\eta\\ \times(\xi+\eta)^{I-L}(\xi-\eta)^{J-L}\,(\xi+1)^k\,(\xi-1)^k\\ \times(\eta+1)^{L-k}\,(\eta-1)^{L-k}\,e^{-\alpha\,r_{12}\,\xi}\,e^{-\beta\,r_{12}\,\eta}.\end{aligned} \tag{4.4.10}$$

This expression can be brought into a more compact form by using the formula

$$(\xi\pm\eta)^j = \sum_{i=0}^{j}\binom{j}{i}(\xi-1)^{j-i}\,(1\pm\eta)^i, \tag{4.4.11}$$

finally giving

$$\begin{aligned}(LM|\hat{\mathcal{K}}|LM) = 2^{-I-J}\pi\sum_{k=0}^{L}\binom{L}{k}^2\sum_{i=0}^{I-L}\binom{I-L}{i}\sum_{j=0}^{J-L}\binom{J-L}{j}(-1)^{i+k+L}\\ \times\int_0^\infty dr_{12}\,r_{12}^{I+J+3}\,\hat{\mathcal{K}}(r_{12})\,A_{k,I-L+J-L-i-j-k}(\alpha\,r_{12})\,B_{L-k+i,L-k+j}(\beta\,r_{12}),\end{aligned} \tag{4.4.12}$$

where the two fundamental integrals are defined as

$$A_{mn}(\alpha) = \int_1^\infty d\xi\,(\xi+1)^m\,(\xi-1)^n\,e^{-\alpha\xi}, \tag{4.4.13}$$

$$B_{mn}(\beta) = \int_{-1}^{+1} d\eta\,(\eta+1)^m\,(1-\eta)^n\,e^{-\beta\eta}. \tag{4.4.14}$$

Note that both integrals are positive independently of the values of the parameters. In order to provide a fully general method, the integration over r_{12} in Eq. (4.4.12) is performed numerically. Let us postpone the discussion of the evaluation of the integrals A_{mn} and B_{mn} and investigate what are the limitations of the method with respect to the functional form of $\hat{\mathcal{K}}(r_{12})$. First, this function cannot be too singular at the origin ($r_{12} = 0$). For small r_{12} the integrals A_{mn} and B_{mn} behave as

$$A_{mn}(\alpha\, r_{12}) = \frac{(n+m)!}{(\alpha\, r_{12})^{n+m+1}} + \mathcal{O}\left(r_{12}^{-n-m}\right), \tag{4.4.15}$$

$$B_{mn}(\beta\, r_{12}) = 2^{m+n+1}\frac{m!\, n!}{(m+n+1)!} + \mathcal{O}\left(r_{12}\right). \tag{4.4.16}$$

Therefore, the integrand in Eq. (4.4.12) without the function $\hat{\mathcal{K}}(r_{12})$ vanishes as $r_{12}^{2L+i+j+2}$ when $r_{12} \to 0$. The integral must be finite for all possible combinations of i, j and L, and the worst-case scenario in this respect is $i = j = L = 0$ which corresponds to the r_{12}^2 term. This allows us to determine that the present method is valid if the function $\hat{\mathcal{K}}(r_{12})$ behaves for small r_{12} as $r_{12}^{-3+\rho}$, where ρ is an arbitrarily small positive constant. Some other types of singularities (e.g. logarithmic) are also allowed but must be integrable after multiplication by r_{12}^2.

A similar analysis can be performed for $r_{12} \to \infty$. We skip a detailed derivation here, but the final conclusion is that the method always works if $\hat{\mathcal{K}}(r_{12})$ vanishes at infinity. If this condition is not satisfied then $\hat{\mathcal{K}}(r_{12})$ must diverge less strongly than $e^{(\alpha-\beta)r_{12}}$, i.e. $\lim_{r_{12}\to\infty} \hat{\mathcal{K}}(r_{12})e^{-(\alpha-\beta)r_{12}} = 0$.

Finally, let us discuss computation of the auxiliary functions A_{mn} and B_{mn}. To facilitate an efficient implementation (which is particularly important if the integral over r_{12} is evaluated numerically) we prefer to use recursive techniques. Additionally, we would like to stress that to improve the numerical stability of the calculations one should avoid expanding the factors $(\xi \pm 1)^m$ with the help of the binomial theorem. This is critical both for A_{mn} and B_{mn}.

Calculation of A_{mn} is rather straightforward. The following recursion allows to bring the first index to zero

$$A_{mn}(\alpha) = A_{m-1,n+1}(\alpha) + 2A_{m-1,n}(\alpha), \tag{4.4.17}$$

at the cost of increasing the second index. Note that the integrals A_{mn} are always positive [cf. Eq. (4.4.13)]. Therefore, the above recursion involves only terms of the same sign and thus is completely stable numerically. To initiate Eq. (4.4.17) one

needs the values of A_{0n}. Fortunately, they can easily be integrated with elementary methods giving $A_{0n} = e^{-\alpha}\, n!/\alpha^{n+1}$.

Calculation of the second class of integrals is somewhat more complicated. One can express B_{mn} as

$$B_{mn}(\beta) = 2^{m+n+1} \frac{m!\, n!}{(m+n+1)!}\, e^{-\beta} M(n+1, m+n+1, 2\beta), \tag{4.4.18}$$

where $M(a, b, z)$ is the confluent hypergeometric function (denoted as ${}_1F_1$ by some authors). Note that the first two arguments of the hypergeometric function are positive integers while the third argument is an arbitrary real number. To make the latter argument positive one can use the reflection formula $M(a, b, z) = e^z M(b - a, b, -z)$. Calculation of the hypergeometric function $M(a, b, z)$ for positive integers a, b and nonnegative z is discussed in the Appendix of Paper I and this method can be used for calculation of B_{mn} with no changes.

4.5. Non-canonical Slater-type orbitals

4.5.1. Definition and mathematical considerations

In this section we would like to introduce an extension of the standard basis set of Slater-type orbitals given by Eq. (1.4.2). This is achieved by relaxing the former requirement $n > l$ in Eq. (1.4.2). If we set $n = l$ then the following family of orbitals is obtained

$$\bar{\chi}_{lm}(\mathbf{r}; \zeta) := \chi_{llm}(\mathbf{r}; \zeta) = \frac{(2\zeta)^{l+1/2}}{\sqrt{(2l)!}}\, r^{l-1} e^{-\zeta r}\, Y_{lm}(\theta, \phi), \tag{4.5.1}$$

where the notation for all other quantities remains the same. Throughout the thesis we use the name "non-canonical STOs" to denote the orbitals given by Eq. (4.5.1) with $l \geqslant 1$. The orbitals with $l = 0$ ($0s$ orbitals) are disqualified for the reasons detailed further in the text. In the remainder of the sections neglect the normalisation constant in Eq. (4.5.1) for the sake of brevity. Note that there is a substantial difference between the $1p$ orbitals (e.g. $\bar{\chi}_{10}$) and the remaining non-canonical STOs. In fact, the $1p$ orbitals are discontinuous while all other non-canonical STOs are continuous everywhere. This is simple to show by setting $x = y = 0$ in the expression for $1p_z$. One obtains $\operatorname{sgn} z\, e^{-\zeta|z|}$ which is manifestly discontinuous for $z = 0$. Therefore, it is not clear how to calculate the Laplacian of a $1p$ orbital. We clarify

these issues in the remainder of the thesis.

First, one has to ask the question whether the non-canonical STOs constitute a legitimate basis set for quantum chemical calculations. In this subsection we approach the problem from a purely mathematical point of view - the physical significance and usefulness of the non-canonical STOs are discussed further in the thesis. As stated in the introduction, basis set functions used in variational calculations should belong to the first Sobolev space, $W_2^{(1)}(\mathbb{R}^3)$. Therefore, we would like to show first that this is indeed the case for the orbitals given by Eq. (4.5.1). However, instead of evaluating the gradient of Eq. (4.5.1) which is rather messy we can use a different condition. A function $f(\mathbf{r}) \in L^2(\mathbb{R}^3)$ belongs to $W_2^{(1)}(\mathbb{R}^3)$ if $\sqrt{c+k^2}\,\hat{f}(\mathbf{k})$ with some finite $c > 0$ is square integrable [$\hat{f}(\mathbf{k})$ denotes the Fourier transform of $f(\mathbf{r})$]. Therefore, let us first evaluate the Fourier transform of the non-canonical STOs. By the definition

$$\hat{\bar{\chi}}_{lm}(\mathbf{k};\zeta) = \int \frac{d\mathbf{r}}{(2\pi)^{\frac{3}{2}}}\, \bar{\chi}_{lm}(\mathbf{r};\zeta)\, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{4.5.2}$$

To facilitate a straightforward evaluation we prefer to use the plane wave expansion theorem

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l j_l(kr)\, Y_{lm}^*(\theta_\mathbf{r},\phi_\mathbf{r})\, Y_{lm}(\theta_\mathbf{k},\phi_\mathbf{k}), \tag{4.5.3}$$

where $j_l(z)$ are the spherical Bessel functions. By inserting this expression into the above integral and performing elementary integrations over the angles we arrive at

$$\hat{\bar{\chi}}_{lm}(\mathbf{k};\zeta) = \sqrt{\frac{2}{\pi}}\, i^l\, Y_{lm}(\theta_\mathbf{k},\phi_\mathbf{k}) \int_0^\infty dr\, r^{l+1}\, j_l(kr)\, e^{-\zeta r}. \tag{4.5.4}$$

The remaining radial integral can be recognised as a special case of some more general formulae [cf. Eqs. (6.621.1) and/or (8.703) from Ref. [517]]. Additionally, independent derivations of several closely related identities are also available in the literature [306, 344, 518, 346]. Finally, we obtain

$$\hat{\bar{\chi}}_{lm}(\mathbf{k};\zeta) = \sqrt{\frac{2}{\pi}}\, (2ik)^l\, l! \frac{Y_{lm}(\theta_\mathbf{k},\phi_\mathbf{k})}{(\zeta^2+k^2)^{l+1}}. \tag{4.5.5}$$

Returning to our initial problem, we need to show that the following integral is finite

$$\int d\mathbf{k}\,(c+k^2)\,\hat{\bar{\chi}}^*_{lm}(\mathbf{k};\zeta)\,\hat{\bar{\chi}}_{lm}(\mathbf{k};\zeta), \tag{4.5.6}$$

where $c>0$ is an arbitrary finite constant. Again, integration over the angles in the above expression is straightforward leaving

$$\frac{1}{\pi}\,2^{2l+1}\,l!^2\left[c\int_0^\infty dk\,\frac{k^{2l+2}}{(\zeta^2+k^2)^{2l+2}}+\int_0^\infty dk\,\frac{k^{2l+4}}{(\zeta^2+k^2)^{2l+2}}\right]. \tag{4.5.7}$$

As long as we restrict ourselves to the positive real axis, the integrands in the above expression have no singularities and are analytic functions of k. Therefore, to verify whether the integrals exist or not we only need to check the behaviour for $k\to\infty$. For large k the first integrand in Eq. (4.5.7) vanishes as k^{-2l-2} while the second as k^{-2l}. As a result, the first integral exists for every $l>-\frac{1}{2}$ and the second for every $l>\frac{1}{2}$. To conclude, the non-canonical STOs with $l\geqslant 1$ belong to the first Sobolev space $W_2^{(1)}(\mathbb{R}^3)$. However, we have to exclude the $l=0$ case from our considerations ($0s$ orbitals). These functions have no well-defined kinetic energy and cannot be used in variational calculations. Nonetheless, we would like to point out that there are some alternative forms of $0s$ orbitals available in the literature, possibly filling this gap. The following orbitals were first proposed by Green et al. [519] and subsequently used by several other authors [520–523]

$$\sqrt{\frac{ab(a+b)}{2\pi}}\,\frac{1}{a-b}\,\frac{1}{r}\left(e^{-ar}-a^{-br}\right). \tag{4.5.8}$$

One can see that these $0s$ orbitals have no strong singularity as $r\to 0$ [in contrast with $\bar{\chi}_{00}(\mathbf{r};\zeta)$ defined by Eq. (4.5.1)] due to the cancellation between the exponential terms in the brackets. Moreover, in the limit of $a\to b$ we recover the usual $1s$ STOs. It has been shown [523] that a mixed basis set of such $0s$ orbitals and the canonical $1s$ orbitals gives somewhat better energies than the conventional $1s$ basis set with the same number of variational parameters. However, this comes at a cost of considerable difficulties in implementation of the integral program and basis set optimisations. Therefore, we exclude any type of $0s$ orbitals from our further considerations and pretend that no such things as $0s$ orbitals exist.

Finally, let us return to the problem of calculation of the kinetic energy terms within the basis set of non-canonical STOs. In the usual quantum chemical calculations

one requires the following one-electron matrix elements

$$T = \int d\mathbf{r}\, f^*_{l'm'}(\mathbf{r}-\mathbf{R})\, \nabla^2\, \bar{\chi}_{lm}(\mathbf{r};\zeta), \tag{4.5.9}$$

where $f_{l'm'}(\mathbf{r})$ is a function belonging to the first Sobolev space (which may also be a different non-canonical STO). The $1p$ orbitals are particularly problematic here because of their discontinuity. Thus, it is not clear how to evaluate the action of the Laplacian and whether Green's theorem can be applied. In other words, it does not seem obvious whether the kinetic energy operator is Hermitian in this basis. However, we found that all such problems vanish if the non-canonical STOs are consistently interpreted in terms of their Fourier transforms. Since any $f_{l'm'}(\mathbf{r}) \in W_2^{(1)}(\mathbb{R}^3)$ possesses a Fourier transform $\hat{f}_{l'm'}(\mathbf{k})$ we can transform the above matrix element T to the momentum space. This gives

$$T = \int d\mathbf{k}\, \hat{f}^*_{l'm'}(\mathbf{k})\, \hat{\bar{\chi}}_{lm}(\mathbf{k};\zeta)\, k^2\, e^{-i\mathbf{k}\cdot\mathbf{R}} \tag{4.5.10}$$

We assume further that $f_{l'm'}(\mathbf{r})$ have a definite angular momentum and thus can be written in the form $f_{l'm'}(\mathbf{r}) = g_{l'm'}(r)\, Y_{l'm'}(\theta,\phi)$, so that $\hat{f}_{l'm'}(\mathbf{k}) = \hat{g}_{l'm'}(k)\, Y_{lm}(\theta_\mathbf{k},\phi_\mathbf{k})$. This assumption is valid for most basis sets used in practice. Making use of the plane wave expansion theorem and Eq. (4.5.5) we can easily integrate over the angles in the above expression. This leaves a sum of the following radial integrals

$$\int_0^\infty dk\, \frac{k^{l+4}}{(\zeta^2+k^2)^{l+1}}\, \hat{g}^*_{l'm'}(k)\, j_L(kR), \tag{4.5.11}$$

multiplied by simple factors involving the angular momenta of both orbitals. Obviously, these integrals must be finite for the kinetic energy matrix elements T to exist. Since we can assume that $\hat{g}_{l'm'}(k)$ are continuous and finite at $k=0$ we only have to check the behaviour of the integrand at the infinity. At large z the Bessel functions $j_L(z)$ behave as $\frac{1}{z}\sin\left(z-\frac{\pi}{2}L\right)+\mathcal{O}\left(z^{-2}\right)$. Therefore, as k tends to infinity we have

$$\frac{k^{l+4}}{(\zeta^2+k^2)^{l+1}}\, \hat{g}^*_{l'm'}(k)\, j_L(kR) \longrightarrow \frac{1}{R}\sin\left(kR-\frac{\pi}{2}L\right)\frac{\hat{g}^*_{l'm'}(k)}{k^{l-1}}. \tag{4.5.12}$$

Since we are considering the case $l \geqslant 1$ it is sufficient that the functions $\hat{g}^*_{l'm'}(k)$ vanish as k^{-2} or faster for each l'. Under this condition the integrals T exist in the ordinary sense. Importantly, this is satisfied both by the canonical [306, 344, 518, 346] and non-canonical STOs [cf Eq. (4.5.5)], removing the uncertainty about the

evaluation of the kinetic energy matrix elements. This does not mean, of course, that the integrals T have to be evaluated by the series expansion presented above. In fact, more convenient methods (such as the contour integrations with the help of the residue theorem) can be applied to give the same result. The theory presented here should be treated more as a proof of existence rather than a practical solution.

4.5.2. Justification

We are now certain that the non-canonical STOs can be used as a basis set in quantum chemical calculations. It is now time to justify the practical reasons for their introduction. First, let us point out that they appear naturally when the standard (e.g. canonical) STOs are differentiated over the electronic coordinates. For example

$$\partial_z \chi_{100}(\mathbf{r};\zeta) = -\frac{\zeta}{\sqrt{3}}\,\chi_{110}(\mathbf{r};\zeta). \tag{4.5.13}$$

Therefore, the derivative of the simplest $1s$ STO is a $1p$ orbital. Similarly, by differentiation of STOs with higher quantum numbers one obtains $2d$, $3f$, ... orbitals as one of the terms. Let us show how this property manifests itself in some nontrivial practical problems.

Suppose we were given a solution $\tau(\mathbf{r})$ of some effective one-electron Schrödinger equation

$$\left(\hat{h}_{\text{eff}} - \epsilon\right)\tau(\mathbf{r}) = 0. \tag{4.5.14}$$

The goal here is to calculate the quantity $\nabla\tau(\mathbf{r})$. If $\tau(\mathbf{r})$ is expanded in some one-particle basis set then the problem seems to be trivial as the differentiation can be performed analytically. However, this may not always be the case. The solution $\tau(\mathbf{r})$ can have a very complicated form or be given in a purely numerical fashion (e.g. on a grid). Additional difficulties arise when many-electron wavefunctions are considered with help of, e.g. coupled cluster methods. All problems can be avoided if the above effective Schrödinger equation is differentiated instead giving

$$\left(\hat{h}_{\text{eff}} - \epsilon\right)[\nabla\tau(\mathbf{r})] = -\left[\nabla, \hat{h}_{\text{eff}}\right]\tau(\mathbf{r}), \tag{4.5.15}$$

and the solution $\nabla\tau(\mathbf{r})$ is expanded in some basis set. If the interactions between the particles (e.g. between the electron and the nuclei) are given by the standard

Coulomb potential (at least for small r) then $\tau(\mathbf{r})$ has a cusp at the coalescence points. Therefore, the basis set used for the expansion of $\nabla\tau(\mathbf{r})$ must be able to describe a derivative of this feature. In face of the arguments presented at the beginning of this section, the simplest way to achieve this goal is to explicitly include the non-canonical STOs into the basis set used for $\nabla\tau(\mathbf{r})$. Of course, if a basis set composed of canonical STOs was used for this purpose the correct result would be obtained in the completeness limit. However, the efficiency of the standard basis sets can be expected to be poor in the case of $\nabla\tau(\mathbf{r})$. A much more robust, albeit more complicated, solution is to incorporate the non-canonical STOs for this task. This is especially true if high accuracy of the results is required.

From the above discussion one can derive a wrong impression that the feature given by Eq. (4.5.13) is an inherent disadvantage of STOs, greatly complicating their application to problems similar to the above simple example. In fact, let us compare this situation with the Gaussian-type orbitals. The analogue of Eq. (4.5.13) is elementary, $\partial_z\, e^{-\alpha r^2} = -2\alpha\, z\, e^{-\alpha r^2}$. In other words, a derivative of an s-type GTO is a p-type GTO which can readily be included in the calculations without any difficulties. However, let us now consider how the exact solutions of Eq. (4.5.14) behave for small r. For the clarity of the presentation we restrict ourselves here to the spherically symmetric solutions, but a similar analysis can be performed in the general case. Up to a trivial multiplicative factor one has

$$\tau(\mathbf{r}) = 1 + \kappa r + \mathcal{O}(r^2), \tag{4.5.16}$$

where κ is a system-dependent constant. Therefore, for the derivative one obtains

$$\nabla\tau(\mathbf{r}) = \mathbf{r}\left[\frac{\kappa}{r} + \mathcal{O}(r)\right]. \tag{4.5.17}$$

If a basis set composed of s-type GTOs is used for the expansion of $\tau(\mathbf{r})$ then (for small r) one attempts to approximate r by a linear combination of $e^{-\alpha r^2}$. Similarly, if the $2p$-type GTOs are used for $\nabla\tau(\mathbf{r})$ then one tries to represent $\frac{\mathbf{r}}{r}$ in terms of $\mathbf{r}\, e^{-\alpha r^2}$. If the former task is difficult and sub-optimal (as it is well-known) then the latter is abysmal. To conclude, the fact that a derivative of a GTO is simple and can be used as a basis set function without any difficulties does not mean that it approximates the actual target function with any reasonable accuracy.

To finalise the present section we note that our interest in the non-canonical STOs was sparked mainly by the problem of calculation of several post-Born-Oppenheimer

effects. This includes, e.g. the adiabatic correction or some quantities appearing in the QED terms such as the Bethe logarithm.

4.5.3. Matrix elements

The use of extended basis set (4.5.1) causes some problems in the evaluation of the resulting matrix elements. These difficulties originate from the fact that the power of r in Eq. (4.5.1) is artificially lowered. Therefore, in contrast to the ordinary STOs, it is impossible to rewrite the orbital (4.5.1) is terms of a regular solid harmonic multiplied by an exponential function. The additional inverse power of r produces apparent singularities which have to be removed, producing somewhat more complicated formulae. To address these issues, in this section we discuss the evaluation of the matrix elements necessary to perform calculations with the basis set functions (4.5.1).

In practical applications one would like to use the conventional STOs basis sets augmented by a sufficient number of non-canonical STOs. This approach appears to be the most reasonable because of two main reasons. First, by adding only a relatively small number of non-canonical STOs the whole basis set does not need to be re-optimised. Only few exponents of the non-canonical STOs must be found which is much more robust. Second, by composing a basis set of a considerable number of both the conventional (e.g. canonical) STOs and non-canonical STOs one faces the risk of an over-completeness. This may result in severe linear dependencies within the basis set, negatively impacting the numerical stability and convergence properties of the electronic structure calculations. However, independently of the adopted strategy, methods of calculation of the STOs matrix elements need to be extended to incorporate the case when the conventional and non-canonical STOs are used simultaneously.

Since the evaluation of the one-electron matrix elements with the non-canonical STOs is a relatively straightforward task and requires only minor extensions, we jump to the two-electron quantities straight away. Here, we have to distinguish between the Coulomb, hybrid, and exchange cases. Typically, the exchange integrals are the most difficult quantities appearing in calculations for diatomic molecules. Somewhat ironically, in the present context they constitute the simplest case. To justify this statement, we have to take a look at Eq. (9) from Paper I. One can see that when the first non-canonical STOs is located at the centre A and the second at the centre B there is an apparent singularity $\frac{1}{r_a\, r_b}$ in the product. The remainder

is transferred to the ellipsoidal coordinates with help of Eq. (7) from Paper I and causes no problems. Fortunately, this singularity is automatically cancelled by the Jacobian standing in front of Eq. (9) from Paper I by the virtue of an obvious expression, $r_a\, r_b = \frac{1}{4}R^2\,(\xi^2 - \eta^2)$. Therefore, to transfer the product of two non-canonical STOs located at different centres to the ellipsoidal coordinates one only has to rearrange Eq. (9) from Paper I so that the volume element is not included in the coefficients $\Xi^M_{l_a l_b}$. Instead, the volume element is rewritten as $\frac{1}{8}R^3\,(\xi^2 - \eta^2) = \frac{2}{R} r_a\, r_b$ and used to cancel the singularity generated by the orbitals product. A very similar approach can be used when one of the orbitals is a standard STO and the second is a non-canonical STO. To sum up, if the exchange integrals are calculated with help of the Neumann expansion the non-canonical STOs can be used without great complications. It suffices to slightly modify the method by which the orbital products are transferred to the ellipsoidal coordinates. This is now done by default in our integral program.

Taking into consideration the arguments presented in the previous paragraph one can now understand why the exchange integrals with the non-canonical STOs are relatively elementary to compute but the Coulomb and hybrid cases pose a more serious challenge. Indeed, if both orbitals from the previous example were located at the same centre (A, say) we would encounter a singularity $1/r_a^2$ instead of $\frac{1}{r_a\, r_b}$. The former singularity is only partially cancelled by the volume element, leaving a remainder proportional to r_b/r_a which cannot be transferred to the ellipsoidal coordinates with standard relations. Therefore, for a product of two orbitals with a common centre a different approach has to be used.

The starting point in calculation of the standard Coulomb and hybrid integrals is the relation (17) from Paper I, allowing for a straightforward integration over coordinates of one of the electrons. When both orbitals dependent on the coordinates of the same electron are non-canonical STOs the left-hand-side of Eq. (17) from Paper I must include the case $L_2 = n_{34}$. Unfortunately, Eq. (17) is invalid under these conditions. This is blatantly visible in the factorial term since $(-1)!$ has no meaning in the present context. Therefore, we require a new analytic expression which covers this special case. More precisely, we need to consider the following integral

$$\mathcal{A}_L = \int d\mathbf{r}_2\, \frac{1}{r_{12}}\, r_{2b}^{L-2}\, Y_{LM}(\cos\theta_{2b}, \phi)\, e^{-\zeta r_{2b}}, \tag{4.5.18}$$

where the notation is the same as in Paper I but for the sake of brevity we neglected some of the subscripts. The first step in the evaluation of Eq. (4.5.18) is to transform the integral to the spherical coordinates and insert the Laplace expansion of the $\frac{1}{r_{12}}$ potential. After elementary integration over the angles one arrives at

$$\mathcal{A}_L = \frac{4\pi}{2L+1} Y_{LM}(\cos\theta_{1b}, \phi) \int_0^\infty dr_{2b}\, r_{2b}^L \frac{r_<^L}{r_>^{L+1}} e^{-\zeta r_{2b}}, \tag{4.5.19}$$

where $r_< = \min\left(r_{1b}, r_{2b}\right)$ and $r_> = \max\left(r_{1b}, r_{2b}\right)$. By dividing the integration interval into two parts, $[0, r_{1b}]$ and $[r_{1b}, \infty)$, one obtains the result

$$\mathcal{A}_L = \frac{4\pi}{2L+1} r_{1b}^L Y_{LM}(\cos\theta_{1b}, \phi)\Big[a_{2L}(\zeta r_{1b}) + A_{-1}(\zeta r_{1b})\Big], \tag{4.5.20}$$

where A_n and a_n are defined by Eqs. (10) and (12) in Paper I. Note that A_{-1} is usually called the exponential integral (denoted E_1 or Ei) but we would like to preserve the consistent notation of Paper I here.

The above expression is a strict counterpart of Eq. (17) from Paper I and can be used to evaluate the analogues of Eqs. (15) and (16) from Paper I with $n_{34} = L_2$. Here, we consider only the case of the Coulomb integrals - the corresponding expressions for the hybrid matrix elements are obtained by using exactly the same methodology. By setting $n_{34} = L_2$ in Eq. (15) from Paper I, inserting Eq. (4.5.20) and rearranging one obtains

$$\begin{aligned}\widetilde{I}_C = \frac{4\pi}{2L_2+1} \int d\mathbf{r}_1\, r_{1a}^{n_{12}-2}\, Y_{L_1M}^*(\cos\theta_{1a}, \phi)\, e^{-\zeta_{12} r_{1a}}\, r_{1b}^{L_2} \\ \times Y_{L_2M}(\cos\theta_{1b}, \phi)\Big[a_{2L_2}(\zeta_{34} r_{1b}) + A_{-1}(\zeta_{34} r_{1b})\Big].\end{aligned} \tag{4.5.21}$$

At this point we would like to temporarily deviate from our main topic and introduce a different method of transferring the product of two STOs (both conventional and non-canonical) to the ellipsoidal coordinates. To the best of our knowledge, this method has not appeared in the literature thus far and constitutes a novel result. From a purely mathematical point of view, the new method is entirely equivalent to the conventional treatment given by Eq. (9) in Paper I. The only difference is that it leads to somewhat different basic quantities and involves some rearrangements of terms. However, we found that the new scheme possesses several superior practical advantages. Most importantly, it is much more numerically stable and avoids sizeable cancellations of significant digits for larger quantum numbers and/or some values

of the exponents. This is especially true for products of two STOs with the same magnetic quantum numbers (m) - a special case of particular importance for the Coulomb and hybrid integrals, cf. Eq. (4.5.21). The new transformation formula reads

$$\begin{aligned} & r_a^{n_a-1} e^{-\zeta_a r_a}\, Y^*_{l_a m}(\cos\theta_a,\phi)\, r_b^{n_b-1} e^{-\zeta_b r_b}\, Y_{l_b m}(\cos\theta_b,\phi) = \\ & (-1)^{l_a+l_b} \left(\frac{R}{2}\right)^{n_a+n_b+1} \Omega_{l_a m}\, \Omega_{l_b m}\, p_{l_a m}\, p_{l_b m} \sum_{i_a=m}^{l_a} F_{i_a}^{l_a m} \sum_{i_b=m}^{l_b} F_{i_b}^{l_b m}\, (-1)^{i_a+i_b} \\ & \times \sum_{j_a=0}^{n_a-l_a} \binom{n_a-l_a}{j_a} \sum_{j_b=0}^{n_b-l_b} \binom{n_b-l_b}{j_b} (\xi+1)^{i_a+i_b-m}\, (\xi-1)^{n_a+n_b+m-i_a-i_b-j_a-j_b} \\ & \times (1+\eta)^{l_b-i_b+i_a+j_b}\, (1-\eta)^{l_a-i_a+i_b+j_b}\, e^{-\alpha\xi}\, e^{-\beta\eta}, \end{aligned} \tag{4.5.22}$$

where Ω_{lm} are defined by Eq. (4) in Paper I, $p_{lm} = 2^{-l}\sqrt{\frac{2l+1}{2}\binom{l+m}{l-m}\frac{(2m)!}{m!^2}}$, $F_i^{lm} = \binom{l}{i}\binom{l}{i-m}$, and α, β have the same meaning as in Eq. (9) of Paper I. Derivation of this expression involves some tedious algebra and is not included here. However, we list a handful of formulae which constitute the most important elements of the new transformation scheme, i.e.

$$P_l^m(\cos\theta) = p_{lm} \left(1-\cos^2\theta\right)^{m/2} \sum_{i=m}^{l} F_i^{lm}\, (\cos\theta+1)^{i-m}\, (\cos\theta-1)^{l-i}, \tag{4.5.23}$$

$$\cos\theta_a \pm 1 = \frac{(1\pm\xi)(1\pm\eta)}{\xi+\eta}, \quad \cos\theta_b \pm 1 = \frac{(1\pm\xi)(1\mp\eta)}{\xi-\eta}. \tag{4.5.24}$$

Additionally, Eq. (4.4.11) is useful is bringing the expression (4.5.22) into its final form. Note that Eq. (4.5.22) remains well-defined for the non-canonical STOs as a special case, i.e. for $n_a = l_a$ and/or $n_b = l_b$.

Let us now return to the Coulomb integrals given by Eq. (4.5.21). Here, we have to distinguish between two possible cases, namely $n_{12} = L_1$ and $n_{12} > L_1$. The other possible combinations do not correspond to any physically acceptable combination of orbitals. The former case occurs when both orbitals dependent on the coordinates of the first electron [cf. Eq. (13) from Paper I] are non-canonical STOs. The latter case covers the opposite situation - at least one of the orbitals is a canonical STO. Let us note that for the hybrid integrals only the second combination is possible so that no branching in the computer program is required .

Starting with the simpler case $n_{12} > L_1$ one can see that the new transformation formula (4.5.22) can be used rather straightforwardly. This allows to express the fundamental Coulomb integral (4.5.21) as a linear combination of the following quantities

$$\begin{aligned} U_{ij}^{kl}(L;\alpha,\beta,\gamma) = \int_1^\infty d\xi \int_{-1}^{+1} d\eta\, (\xi+1)^i\, (\xi-1)^j\, (1+\eta)^k\, (1-\eta)^l \\ \times \Big\{ a_L[\gamma(\xi-\eta)] + A_{-1}[\gamma(\xi-\eta)] \Big\}\, e^{-\alpha\xi}\, e^{-\beta\eta}. \end{aligned} \tag{4.5.25}$$

To evaluate these integrals we pursue the strategy introduced in Paper I, i.e. rewrite them as simpler one-dimensional integrals and perform the last integration numerically. The first step is to recognise the following representations

$$a_L[\gamma(\xi-\eta)] = \int_0^1 dx\, x^L\, e^{-\gamma(\xi-\eta)x}, \tag{4.5.26}$$

$$A_{-1}[\gamma(\xi-\eta)] = \int_0^1 \frac{dx}{x}\, e^{-\gamma(\xi-\eta)/x}. \tag{4.5.27}$$

Next, both these expressions are inserted into Eq. (4.5.25) and the integrations over x are brought to the front. Finally, the inner integrals over ξ and η are expressed through the fundamental quantities given by Eqs. (4.4.13) and (4.4.14). This gives us the final expression

$$\begin{aligned} U_{ij}^{kl}(L;\alpha,\beta,\gamma) = \int_0^1 dx \Big[x^L A_{ij}(\alpha+\gamma x)\, B_{kl}(\beta-\gamma x) \\ + \frac{1}{x} A_{ij}(\alpha+\gamma/x)\, B_{kl}(\beta-\gamma/x) \Big], \end{aligned} \tag{4.5.28}$$

which is suitable for a numerical treatment. As discussed in the previous sections, the basic integrals A_{mn} and B_{mn} can be evaluated with a controlled precision for arbitrary values of the arguments. Note that numerical calculation of the above integral is not significantly more expensive than of the standard Coulomb matrix elements, cf. Eq. (26) in Paper I. Our initial tests show that this introduces an overhead by only a factor of two which is still an acceptable cost.

Now we turn our attention to the more problematic $n_{12} = L_1$ case of Eq. (4.5.21). The biggest difficulty here is the apparent singularity of the $r_{1a}^{L_1-2}$ term. This prevents a straightforward application of the transformation formula, Eq. (4.5.22). Because we lack any other options we rewrite the troublesome term $r_{1a}^{L_1-2}$ as $r_{1a}^{L_1-1}\frac{1}{r_a}$. Next,

the $\frac{1}{r_a}$ singularity is temporarily left out and the transformation (4.5.22) is applied to the remainder of the integrand. As a result, the integrals (4.5.21) with $n_{12} = L_1$ can be rewritten as linear combinations of

$$V_{ij}^{kl}(L;\alpha,\beta,\gamma) = \int_1^\infty d\xi \int_{-1}^{+1} d\eta\, (\xi+1)^i\,(\xi-1)^j\,(1+\eta)^k\,(1-\eta)^l \times \Big\{a_L[\gamma(\xi-\eta)] + A_{-1}[\gamma(\xi-\eta)]\Big\}\, e^{-\alpha\xi}\, e^{-\beta\eta}\frac{1}{\xi+\eta}, \tag{4.5.29}$$

where the last term comes from separate transformation of the $\frac{1}{r_a}$ singularity. By using similar tricks as in the previous case the above expression can be formally rewritten as a one-dimensional integral

$$V_{ij}^{kl}(L;\alpha,\beta,\gamma) = \int_0^1 dx \left[x^L\, v_{ij}^{kl}(\alpha+\gamma x, \beta-\gamma x) + \frac{1}{x}\, v_{ij}^{kl}(\alpha+\gamma/x, \beta-\gamma/x)\right], \tag{4.5.30}$$

where the quantities under the integral sign are given by

$$v_{ij}^{kl}(a,b) = \int_1^\infty d\xi \int_{-1}^{+1} d\eta\, (\xi+1)^i\,(\xi-1)^j\,(1+\eta)^k\,(1-\eta)^l\, e^{-a\xi}\, e^{-b\eta}\frac{1}{\xi+\eta}. \tag{4.5.31}$$

One can see that $v_{ij}^{kl}(a,b)$ do not separate into products of simple one-dimensional integrals due to presence of the $\frac{1}{\xi+\eta}$ factor. However, assuming the integrals $v_{ij}^{kl}(a,b)$ were evaluated analytically with a reasonable efficiency and controlled precision nothing would prevent us from integrating over x numerically. Further in the thesis we adopt this pragmatic approach.

Let us begin by noting that the integrals $v_{ij}^{kl}(a,b)$ obey two simple recursion relations

$$v_{i+1,j}^{kl}(a,b) = v_{i,j+1}^{kl}(a,b) + 2\, v_{ij}^{kl}(a,b), \tag{4.5.32}$$

$$v_{i,j+1}^{kl}(a,b) = A_{ij}(a)\, B_{kl}(b) - v_{ij}^{k+1,l}(a,b). \tag{4.5.33}$$

The first recursion is elementary to derive and involves only terms of the same sign since $v_{ij}^{kl}(a,b) > 0$. Therefore, it is completely stable numerically. The second relation

is a consequence of the following basic identity

$$1 = \frac{\xi - 1}{\xi + \eta} + \frac{1 + \eta}{\xi + \eta}. \tag{4.5.34}$$

Note that Eq. (4.5.33) involves a subtraction, so that a loss of digits is possible during the evaluation. However, the integrals $v_{ij}^{kl}(a,b)$ typically increase with i, j, and decrease with k, l. This makes the relation (4.5.33) very stable numerically and our tests show that the cancellations on the right-hand-side of Eq. (4.5.33) are insignificant. Overall, the bottom line here is that the recursions (4.5.32) and (4.5.33) allow to calculate the integrals $v_{ij}^{kl}(a,b)$ starting only with $v_{00}^{kl}(a,b)$ which is a major simplification.

With i and j reduced to zero one can now easily perform the integration over ξ in $v_{00}^{kl}(a,b)$. This gives the following representation

$$v_{00}^{kl}(a,b) = -e^{a-b} \int_0^2 dx\, (2-x)^k\, x^l\, e^{-x(a-b)}\, \mathrm{Ei}(-ax), \tag{4.5.35}$$

where Ei is the ordinary exponential integral function. The next step is to recognise the recursion

$$v_{00}^{k+1,l}(a,b) = 2\, v_{00}^{kl}(a,b) - v_{00}^{k,l+1}(a,b), \tag{4.5.36}$$

which brings down the value of k to zero. Unfortunately, in contrast with the analogous relation (4.5.32) this recursion is not fully numerically stable. This is the weakest point in the proposed procedure and further research is necessary to resolve this problem. Nonetheless, the use of Eq. (4.5.36) is a reasonable approach for small quantum numbers.

Finally, we need to handle the last integrals class, $v_{00}^{0l}(a,b)$. The values of l can be increased by consecutive differentiations over b

$$v_{00}^{0l}(a,b) = -e^{a-b}\, \partial_b^l \int_0^2 dx\, e^{-x(a-b)}\, \mathrm{Ei}(-ax) = e^{a-b}\, \partial_b^l\, I_0(a,b) = e^{a-b}\, I_l(a,b). \tag{4.5.37}$$

The simplest integrals $I_0(a,b)$ are solved with elementary methods and we obtained the following closed-form expression

$$(a-b)\, I_0(a,b) = f_0(2b) + e^{2b} \log 2a - e^{2a}\, \mathrm{Ei}(-2a), \tag{4.5.38}$$

where

$$f_0(x) = e^x \Big[\mathrm{Ei}(-x) - \log |x| \Big]. \tag{4.5.39}$$

The exponential integral is understood as the Cauchy principal value for $x < 0$. If we define $f_n(x) = \partial_x^n \, f_0(x)$ then it becomes trivial to differentiate both sides of Eq. (4.5.38) with respect to b. This gives a convenient recursion relation for $I_n(a,b)$

$$(a-b)\, I_n(a,b) = n\, I_{n-1}(a,b) + 2^n \Big[f_n(2b) + e^{2b} \, \log 2a - \delta_{n0} \, e^{2a} \, \mathrm{Ei}(-2a) \Big], \tag{4.5.40}$$

which is self-starting provides that the first term on the right-hand-side is neglected for $n = 0$ (δ_{mn} is the usual Kronecker delta symbol). We found this relation to be surprisingly numerically stable for all values of a and b with only one or two digits lost even for quite large n.

The last piece of the puzzle is evaluation of the auxiliary quantities $f_n(x)$. The method we propose here differs for positive and negative x. For $x > 0$ the following recursion relation is adequate

$$f_{n+1}(x) = f_n(x) - a_n(-x), \tag{4.5.41}$$

where a_n are defined by Eq. (12) in Paper I. Because the values of $f_n(x)$ with $n > 0$ and $x > 0$ are negative, and $a_n(x) > 0$ everywhere this recursion is always numerically stable. The remaining problem is evaluation of the exponential integral (minus the logarithm) on the negative real axis which is necessary for $f_0(x)$. This problem has been discussed in the literature numerous times and numerically satisfactory procedure are available [524–528]. For negative x the values of $f_n(x)$ can be evaluated by series expansions. For example, in the $n = 0$ case we have

$$f_0(-x) = e^{-x} \Big[\gamma + \sum_{n=1}^{\infty} \frac{x^k}{k k!} \Big], \tag{4.5.42}$$

and larger n can be obtained by differentiation. The most important aspect of this expression is that the summation involves only positive terms and thus it is completely stable against the round-off errors. It converges slowly for large x but can be used up to a point where the asymptotic expansions of Ei can be applied.

In the above presentation we have tacitly assumed that $a \neq b$. Unfortunately, the case of $a = b$ is physically acceptable (e.g. for equal screening constants of STOs)

and the recursion (4.5.40) cannot be used then. Therefore, a dedicated method is necessary for $a = b$. As a bonus, one can also treat the integrals with $a \approx b$ by expanding around $a = b$. Since the recursions (4.5.32), (4.5.33), and (4.5.36) are valid for $a = b$ we have to solve $v_{00}^{0l}(a,a)$ with $a > 0$. From the definition

$$v_{00}^{0l}(a,a) = -\int_0^2 dx\, x^l\, \mathrm{Ei}(-ax). \tag{4.5.43}$$

Integration by parts gives the following closed-form expression

$$v_{00}^{0l}(a,a) = \frac{2^{l+1}}{l+1}\Big[-\mathrm{Ei}(-2a) + a_l(2a)\Big]. \tag{4.5.44}$$

Both terms in the square brackets all positive for all l and thus no cancellations are possible in the evaluation. This completes the method for calculation of $v_{ij}^{kl}(a,b)$.

To finalise the present section we consider the evaluation of the atomic integrals with the non-canonical STOs. This task is much more elementary than in the case of the Coulomb and hybrid integrals but we decided to discuss this issue for the sake of completeness. Similarly as in the Supplemental Material to Paper I we define the atomic integrals as

$$\begin{aligned} I_A = &\int d\mathbf{r}_1 \int d\mathbf{r}_2\, \chi^*_{n_1 l_1 m_1}(\mathbf{r}_1;\zeta_1)\, \chi_{n_2 l_2 m_2}(\mathbf{r}_1;\zeta_2) \\ &\times \frac{1}{r_{12}}\, \chi^*_{n_3 l_3 m_3}(\mathbf{r}_2;\zeta_3)\, \chi_{n_4 l_4 m_4}(\mathbf{r}_2;\zeta_4), \end{aligned} \tag{4.5.45}$$

but this time we relax the previously imposed requirement $n_i > l_i$ and allow that some (or all) of the orbitals under the integral sign are non-canonical STOs. The first step in evaluation of Eq. (4.5.45) is to use the Laplace expansion of the interaction potential, $\frac{1}{r_{12}}$. This allows to integrate over the solid angles of both electrons giving

$$\begin{aligned} I_A = &(-1)^{m_1+m_3} \sqrt{\prod_{i=1}^{4}(2l_i+1)} \sum_L \begin{pmatrix} l_1 & L & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_3 & L & l_4 \\ 0 & 0 & 0 \end{pmatrix} \\ &\times \Big[R_L(n_{12}, n_{34}; \zeta_{12}, \zeta_{34}) + R_L(n_{34}, n_{12}; \zeta_{34}, \zeta_{12}) \Big] \\ &\times \sum_{M=-L}^{L} (-1)^M \begin{pmatrix} l_1 & L & l_2 \\ -m_1 & -M & m_2 \end{pmatrix} \begin{pmatrix} l_3 & L & l_4 \\ -m_3 & M & m_4 \end{pmatrix}, \end{aligned} \tag{4.5.46}$$

where $n_{12} = n_1 + n_2$, $\zeta_{12} = \zeta_1 + \zeta_2$, and an analogous notation is used for the quantities related to the second electron. The radial integrals in the square brackets

are given by the formula

$$\begin{aligned} R_L(m,n;a,b) &= \int_0^\infty dr_1\, r_1^{m-L-1}\, e^{-ar_1} \int_0^{r_1} dr_2\, r_2^{n+L}\, e^{-br_2} \\ &= \int_0^\infty dr_2\, r_2^{n+L}\, e^{-br_2} \int_{r_2}^\infty dr_1\, r_1^{m-L-1}\, e^{-ar_1}. \end{aligned} \tag{4.5.47}$$

In the case $m > L$ the above integrals are given by a simple closed-form expression (cf. Supplemental Material to Paper I). However, in the calculations involving non-canonical STOs we also require a special case of $m = L$. First, let us exchange the variables from r_1 to $x = r_1/r_2$ in Eq. (4.5.47). After some rearrangements one obtains

$$R_L(L,n;a,b) = \int_0^\infty dr_2\, r_2^{n+L} e^{-br_2} \int_1^\infty \frac{dx}{x}\, e^{-axr_2} = \int_1^\infty \frac{dx}{x}\, \frac{(n+L)!}{(ax+b)^{n+L+1}}. \tag{4.5.48}$$

The above integral can be rewritten shortly as

$$R_L(L,n;a,b) = a^{-n-L-1} \widetilde{R}_{n+L}\left(\frac{a}{b}\right), \quad \text{with} \quad \widetilde{R}_k(x) = k!\, x^{k+1} \int_x^\infty \frac{dt}{t}\, (t+1)^{-k-1}. \tag{4.5.49}$$

The latter quantity obeys a straightforward recursion relation

$$\widetilde{R}_k(x) = \frac{k!}{k+1}\left(\frac{x}{x+1}\right)^{k+1} + \frac{1}{x(k+1)} \widetilde{R}_{k+1}(x). \tag{4.5.50}$$

This recursive process is unstable in the upward direction (i.e. increasing k). However, for small values of k this is not expected to be a problem and the starting value is simply $\widetilde{R}_0(x) = x \ln \frac{x}{x+1}$. If larger values of k are required then the recursion must be carried in the downward direction. One starts with $\widetilde{R}_K(x) = 0$ at some large K - larger than the maximal value of k actually desired. The accuracy of this initial approximation quickly improves with decreasing k.

4.6. Geometric derivatives

4.6.1. Justification

In this section we consider the calculation of the geometric derivatives, i.e. derivatives of the STOs matrix elements with respect to the nuclear coordinates. The latter can be defined either through the Cartesian coordinates of all the nuclei or

through some internal coordinates. In the case of the diatomic systems this trivialises to a single variable - the internuclear distance, R.

Geometric derivatives of various quantities (e.g. molecular energies) are of prime importance in quantum chemistry. They allow to find molecular equilibrium geometries, transition states of chemical reactions, harmonic vibrational frequencies of polyatomic systems etc. [553] Thus, very powerful analytic differentiation techniques were developed for many quantum chemistry methods [554–560]. However, for diatomic systems the task of finding a minimum of the potential energy curve can be accomplished much easier and geometric gradient methods are rarely employed. Moreover, the whole potential energy curve is typically required in serious studies. It does not mean, however, that the geometric derivatives of the matrix elements are of no use for the diatomic systems. Let us illustrate this statement by a simple example. For a homonuclear diatomic system the adiabatic correction reads [561–566]

$$E_a = \frac{1}{2\mu}\Big[\langle \partial_R \Psi | \partial_R \Psi \rangle + \langle \nabla \Psi | \nabla \Psi \rangle\Big], \tag{4.6.1}$$

where Ψ is the electronic wavefunction, ∇ is the sum of gradients with respect to the spacial coordinates of all electrons, and μ is the reduced nuclear mass. Probably the simplest way to obtain the quantity $\partial_R \Psi$ is to differentiate the electronic Schrödinger equation ($H\Psi = E\Psi$) with respect to R. After simple rearrangements one arrives at

$$(H - E)\partial_R \Psi = \Big[H, \partial_R\Big]\Psi + (\partial_R E)\,\Psi, \tag{4.6.2}$$

which must be solved for $\partial_R \Psi$. Let us consider the first term on the right-hand-side of the above equation. If one assumes that the Hamiltonian is given in the usual first-quantised form then the only non-vanishing term in the commutator comes from the nuclear potential and is relatively simple. However, this is equivalent to the assumption that the electronic Schrödinger equation has been solved exactly. Apart from a few methods applicable mostly to small systems [566–568] this is rarely a good approximation. A more consistent approach is to rewrite the Hamiltonian in the second-quantised form within the given one-electron basis and perform the explicit differentiation. While this approach is justified even for approximate electronic structure methods, it leads to geometric derivatives of the one- and two-electron integrals appearing in the second-quantised representation of the Hamiltonian. Calculation of these quantities within the basis set of STOs is the subject of the present section.

4.6.2. One-electron integrals

Let us begin by considering the simplest overlap integrals. Obviously, when both orbitals are located on the same centre the derivative of the overlap integral vanishes, i.e. $\partial_R(a|a) = \partial_R(b|b) = 0$. Therefore, we only need to consider the case $(a|b)$. According to Eqs. (4.5.22), (4.4.13) and (4.4.14) we have

$$\begin{aligned}
&\int d\mathbf{r}\; \chi^*_{n_a l_a m}(\mathbf{r}_a;\zeta_a)\, \chi_{n_b l_b m}(\mathbf{r}_b;\zeta_b) = \\
&\left(\frac{R}{2}\right)^{n_{ab}+1} \sum_{i_a=m}^{l_a} F_{i_a}^{l_a m} \sum_{i_b=m}^{l_b} F_{i_b}^{l_b m}\, (-1)^{i_{ab}} \sum_{j_a=0}^{n_a-l_a} \binom{n_a-l_a}{j_a} \sum_{j_b=0}^{n_b-l_b} \binom{n_b-l_b}{j_b} \\
&\times A_{i_{ab}-m,n_{ab}+m-i_{ab}-j_{ab}}\left[\frac{R}{2}(\zeta_a+\zeta_b)\right] B_{l_b-i_b+i_a+j_b,l_a-i_a+i_b+j_b}\left[\frac{R}{2}(\zeta_a-\zeta_b)\right],
\end{aligned} \tag{4.6.3}$$

where we have adopted a shorthand notation $n_{ab} = n_a + n_b$ etc. and omitted the R-independent multiplicative constants in front of Eq. (4.5.22). One can see that there are only three quantities in this expression which depend on R. The first stands in front of the summations and is trivial to differentiate, generating the initial overlap integral multiplied by a scaling factor. The other two quantities can be differentiated with help of the formulae

$$\partial_\alpha\, A_{mn}(\alpha) = -A_{m,n+1}(\alpha) - A_{mn}(\alpha), \tag{4.6.4}$$

$$\partial_\beta\, B_{mn}(\beta) = B_{m,n+1}(\beta) - B_{mn}(\beta). \tag{4.6.5}$$

A very similar method can be applied to the derivatives of the kinetic energy matrix elements, so we do not list the relevant formulae here.

Let us now pass to the calculation of the derivatives of the matrix elements involving the nuclear attraction. We have eight possible cases of centres location, but for a diatomic system only three are unique, i.e. $(a|a|a)$, $(a|a|b)$, $(a|b|a)$. The remaining integrals can be obtained by renaming the centres a and b, and/or by the complex conjugation of the integrand (all integrals are purely real so the result is unchanged). In the first case we have $\partial_R\,(a|a|a) = 0$. The second case is a modified overlap integral and can be evaluated with a similar scheme as above. The only new

case is $(a|b|a)$. Explicit expression for this integral reads

$$\int d\mathbf{r}\; \chi^*_{n_a l_a m}(\mathbf{r}_a;\zeta_a)\, \chi_{n'_a l'_a m}(\mathbf{r}_a;\zeta'_a)\, \frac{1}{r_b} = (-1)^m \sqrt{(2l_a+1)(2l'_a+1)}\, R^{n_a+n'_a} \sum_{L=|l_a-l'_a|}^{l_a+l'_a} \times \begin{pmatrix} l_a & L & l'_a \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_a & L & l'_a \\ -m & 0 & m \end{pmatrix} \Big[A_{n_a+n'_a-L-1}\left[R(\zeta_a+\zeta'_a)\right] + a_{n_a+n'_a+L}\left[R(\zeta_a+\zeta'_a)\right] \Big], \tag{4.6.6}$$

where A_n and a_n were defined in Paper I. Derivation of this formula is rather straightforward and thus not included here, but can be obtained from authors upon request. By noting the formula $\partial_\alpha A_n(\alpha) = -A_{n+1}(\alpha)$ (which is valid also for a_n) the derivatives of the above expression with respect to R can easily be worked out.

4.6.3. Two-electron integrals

As usual in the treatment of the two-electron STOs integrals we separate them into the atomic, Coulomb, hybrid, and exchange classes. The atomic integrals do not depend on R, so we immediately obtain $\partial_R\,(aa|aa) = \partial_R\,(bb|bb) = 0$. Treatment of the Coulomb and hybrid integrals is virtually the same, so for brevity we consider only the former case here. As shown in Paper I and elaborated in Sec. 4.5 all Coulomb integrals can be rewritten as a linear combination of the basic quantities [cf. Eq. (4.5.22)]

$$U^{kl}_{ij}(L;\alpha,\beta,\gamma) = \int_0^1 dx\, x^L A_{ij}(\alpha+\gamma x)\, B_{kl}(\beta-\gamma x), \tag{4.6.7}$$

where A_{mn} and B_{mn} have been defined through Eqs. (4.4.13) and (4.4.14). The coefficients of the linear combination do not depend on R and the trivial multiplicative factor in front of Eq. (4.5.22) is straightforward to differentiate. The remaining dependence on the internuclear distance is hidden in the parameters α, β, γ. The explicit formula for each parameter in terms of R depends on the location of the orbitals and is quite complicated in the general case. However, we can employ the chain rule

$$\partial_R = \frac{\partial\alpha}{\partial R}\,\partial_\alpha + \frac{\partial\beta}{\partial R}\,\partial_\beta + \frac{\partial\gamma}{\partial R}\,\partial_\gamma, \tag{4.6.8}$$

to derive a general (yet implicit) formula. Differentiation of the functions under the integral sign in Eq. (4.6.7) is rather straightforward and the results read

$$\partial_\alpha A_{ij}(\alpha+\gamma x) = -A_{i,j+1}(\alpha+\gamma x) - A_{ij}(\alpha+\gamma x), \tag{4.6.9}$$
$$\partial_\gamma A_{ij}(\alpha+\gamma x) = -x\Big[A_{i,j+1}(\alpha+\gamma x) + A_{ij}(\alpha+\gamma x)\Big], \tag{4.6.10}$$
$$\partial_\beta B_{kl}(\beta-\gamma x) = B_{k,l+1}(\beta-\gamma x) - B_{kl}(\beta-\gamma x), \tag{4.6.11}$$
$$\partial_\gamma B_{kl}(\beta-\gamma x) = x\Big[B_{k+1,l}(\beta-\gamma x) - B_{kl}(\beta-\gamma x)\Big]. \tag{4.6.12}$$

This leads to the final formulae for the derivatives of the basic integral (4.6.7)

$$\partial_\alpha U_{ij}^{kl}(L;\alpha,\beta,\gamma) = -U_{i,j+1}^{kl}(L;\alpha,\beta,\gamma) - U_{ij}^{kl}(L;\alpha,\beta,\gamma), \tag{4.6.13}$$
$$\partial_\beta U_{ij}^{kl}(L;\alpha,\beta,\gamma) = U_{ij}^{k,l+1}(L;\alpha,\beta,\gamma) - U_{ij}^{kl}(L;\alpha,\beta,\gamma), \tag{4.6.14}$$
$$\begin{aligned}\partial_\gamma U_{ij}^{kl}(L;\alpha,\beta,\gamma) = &-U_{i,j+1}^{kl}(L+1;\alpha,\beta,\gamma) - U_{ij}^{kl}(L+1;\alpha,\beta,\gamma)\\ &+ U_{ij}^{k+1,l}(L+1;\alpha,\beta,\gamma) - U_{ij}^{kl}(L+1;\alpha,\beta,\gamma).\end{aligned} \tag{4.6.15}$$

As a result, derivatives of all Coulomb (and hybrid) integrals can be assembled from the quantities defined above. The latter are expressed through the standard $U_{ij}^{kl}(L;\alpha,\beta,\gamma)$ integrals with some of the indices increased by one.

Finally, we pass to the geometric derivatives of the exchange integrals. As demonstrated by Eq. (3) in Paper II all exchange integrals are linear combinations of two fundamental quantities, $i_\mu^\sigma(q,\beta)$ and $w_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2)$, defined by Eqs. (4) and (6) in Paper II, respectively. Again, we omit the trivial multiplicative constant in front of the transformation formula. The dependence on R is hidden in four variables: α_1, α_2, β_1, and β_2, and the differentiation with respect to R can be simplified with help of the chain rule analogous to Eq. (4.6.8). Now we require only the following elementary relations

$$\partial_{\alpha_1} w_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2) = -w_\mu^\sigma(p_1+1,p_2,\alpha_1,\alpha_2), \tag{4.6.16}$$
$$\partial_{\alpha_2} w_\mu^\sigma(p_1,p_2,\alpha_1,\alpha_2) = -w_\mu^\sigma(p_1,p_2+1,\alpha_1,\alpha_2), \tag{4.6.17}$$
$$\partial_\beta\, i_\mu^\sigma(q,\beta) = -i_\mu^\sigma(q+1,\beta), \tag{4.6.18}$$

which follow straightforwardly from the definitions given in Paper II.

To sum up, geometric derivatives of all two-electron integrals within the STOs basis can be obtained by rather straightforward rearrangements of the initial formulae given in Papers I and II. In particular, no new basic quantities need to be

calculated and the only cost is the increased order of some indices. Therefore, STOs possess no significant disadvantages in this respect as compared with the frequently used GTOs.

CHAPTER 5
Conclusions and outlook

The main goal of the presented thesis has been the development of methods for the calculation of the one- and two-electron matrix elements within the basis set of Slater-type orbitals and subsequent applications to accurate first-principles calculations for the diatomic systems. Such systems are frequently studied, e.g. in the field of ultracold chemistry and physics, and are promising candidates for many future applications. One can safely say that without the theoretical support the progress in many (if not most) experimental studies of the ultracold molecules would stall. This illustrates the importance of developing new theoretical methods of increased accuracy and reliability.

The main achievements of the present work can be summarised as follows:

1. new techniques for the calculation of the standard one- and two-electron matrix elements over STOs have been developed; they have been implemented efficiently and thoroughly tested, proving their superiority over the previous approaches,

2. a systematic and general framework for the design and optimisation of STOs basis sets has been presented, numerous benchmark calculations have been performed and the accuracy of the new basis sets has been critically analysed,

3. matrix elements of various property operators have been implemented which are necessary in calculation of, e.g. the electric multipole moments, nonadiabatic and spin-orbit couplings, leading-order relativistic corrections, and many others - a detailed list is given in Appendix B,

4. the theory of the effective core potentials has been combined with the basis set of Slater-type orbitals allowing for straightforward future applications for

heavy atoms; the spin-orbit and core polarisation potentials have also been implemented,

5. complete potential energy curve for the $a^3\Sigma_u^+$ state of lithium dimer has been calculated with state-of-the-art *ab initio* methods and the basis set of Slater-type orbitals; spectroscopic parameters of this system have been calculated from first principles and compared with the latest experimental data proving that the accuracy of only a few tenths of a wavenumber is attainable within the present approach,

6. full potential energy curve for the ground state of beryllium dimer has been computed with help of the Slater-type orbitals including the relativistic, adiabatic and QED effects; the existence of the weakly bound twelfth vibrational level has been confirmed and a very good agreement with the semi-empirical potentials has been found.

Five research papers published in international scientific journals and two (yet unpublished) preprints constitute the core of the thesis and contain a detailed account of the obtained results. All computer programs written in the course of this work shall be available in the near future for public (non-commercial) use.

We would like to finalise the present thesis by a handful of closing remarks and an outlook for the future. First, let us discuss the immediate applications of the theory presented here to systems of current experimental interest. We plan to utilise the results of the calculations for the $a^3\Sigma_u^+$ state of lithium dimer to search for effects of the QED retardation of the electromagnetic interaction (the Casimir-Polder formula). Prof. Kirk Madison (University of British Columbia, Vancouver, Canada) has recently measured the positions of the rovibrational levels in this state with an unprecedented precision. Unfortunately, the last rovibrational level is still too deeply bound to be sensitive to the influence of the retardation. However, by placing the molecules in the magnetic field (and tuning the field strength) the levels can be pushed upwards almost to the dissociation limit, increasing their sensitivity to this subtle effect. We believe that this is the key to observe the retardation effects in systems larger than the helium dimer.

Another exciting application of the methodology presented in the thesis is the electronic spectra of the barium hydride (BaH) molecule. In Paper V we have shown

that with STOs it is possible to achieve the accuracy of about $20\,\mathrm{cm}^{-1}$ for the ground-state well-depth of approximately $12000\,\mathrm{cm}^{-1}$. We plan to calculate complete potential energy curves for several electronic states of this system with the goal to assist the experimental work currently ongoing in the group of Prof. Tanya Zelevinsky (Columbia University, New York, USA). The main purpose of this project is to establish a new way of generating ultracold hydrogen atoms. This can probably be achieved with the help of laser cooling of the BaH molecules and subsequent photofragmentation into the constituting atoms.

Apart from the immediate applications of the theory put forward in the thesis we plan further developments of the electronic structure methods in conjunction with the basis set of Slater-type orbitals. As detailed in Sec. 4.3, the prospect of employing STOs in the explicitly correlated calculations is very promising. It has been shown that all necessary matrix elements can be calculated efficiently, but the task of developing the required explicitly correlated programs is still challenging. In fact, to push the accuracy of the calculations even further a careful calibration of the methods must be performed and all sources of errors need to be eliminated or tightly controlled. Nonetheless, we believe that with the explicitly correlated techniques the accuracy of the results can be improved at least by an order of magnitude.

Another interesting question related to the present thesis is whether the adopted approach can be extended to larger systems, i.e. many-centre molecules. In fact, we have already made a considerable progress towards this goal and the preliminary results are very promising. While the calculation of the STOs molecular integrals is not going to match the efficiency of the GTOs in a near future, the increase in the accuracy makes up for the computational overhead. A related idea is to augment the standard atom-centred basis set of STOs by including the bond functions or bicentric functions defined in the ellipsoidal coordinates. This is known to significantly improve the description of the chemical bond in the molecular systems.

To conclude, we point out that much can be extended from the results of the present thesis. However, we believe the most important message is that the long-forgotten Slater-type orbitals once again consitute a real alternative for a basis set in quantum chemical calculations.

CHAPTER 6

Appendices

6.1. Appendix A. Exchange integral with r_{12}

$$
\begin{aligned}
(ab|r_{12}|a'b') = 2R\,K_{ab}K_{a'b'} \sum_{k_1=0}^{k_1^{max}} B_{k_1}^{n_1-l_1,n_2-l_2} \sum_{k_2=0}^{k_2^{max}} B_{k_2}^{n_3-l_3,n_4-l_4} \sum_{p_1,q_1=0}^{\Gamma_1} \left(\Xi_{l_1l_2}^{M_1}\right)_{p_1q_1} \sum_{p_2,q_2=0}^{\Gamma_2} \left(\Xi_{l_3l_4}^{M_2}\right)_{p_2q_2} \\
\Bigg[\delta_{M_1,-M_2}\,\delta_{\sigma,|M_2|}(-1)^{\sigma} \sum_{\mu=\sigma}^{\infty}(2\mu+1)\Big[W_\mu^\sigma(p_1+k_1+2,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1,\beta_1) \\
\times i_\mu^\sigma(q_2+k_2^{max}-k_2,\beta_2) + W_\mu^\sigma(p_1+k_1,p_2+k_2+2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1,\beta_1) \\
\times i_\mu^\sigma(q_2+k_2^{max}-k_2,\beta_2) + W_\mu^\sigma(p_1+k_1,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1+2,\beta_1) \\
\times i_\mu^\sigma(q_2+k_2^{max}-k_2,\beta_2) + W_\mu^\sigma(p_1+k_1,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1,\beta_1) \\
\times i_\mu^\sigma(q_2+k_2^{max}-k_2+2,\beta_2) - 2W_\mu^\sigma(p_1+k_1,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1,\beta_1) \\
\times i_\mu^\sigma(q_2+k_2^{max}-k_2,\beta_2) - 2W_\mu^\sigma(p_1+k_1+1,p_2+k_2+1,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1+1,\beta_1) \\
\times i_\mu^\sigma(q_2+k_2^{max}-k_2+1,\beta_2)\Big] + \delta_{M_2,-M_1-2}\,\delta_{\sigma,|M_2+1|}(-1)^{\sigma} \sum_{\mu=\sigma}^{\infty}\sum_{\mu=\sigma}^{\infty}(2\mu+1) \\
\Big[W_\mu^\sigma(p_1+k_1,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1,\beta_1)\,i_\mu^\sigma(q_2+k_2^{max}-k_2,\beta_2) \\
- W_\mu^\sigma(p_1+k_1,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1+2,\beta_1)\,i_\mu^\sigma(q_2+k_2^{max}-k_2,\beta_2) \\
- W_\mu^\sigma(p_1+k_1,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1,\beta_1)\,i_\mu^\sigma(q_2+k_2^{max}-k_2+2,\beta_2) \\
+ W_\mu^\sigma(p_1+k_1,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1+2,\beta_1)\,i_\mu^\sigma(q_2+k_2^{max}-k_2+2,\beta_2) \\
- W_\mu^\sigma(p_1+k_1+2,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1,\beta_1)\,i_\mu^\sigma(q_2+k_2^{max}-k_2,\beta_2) \\
+ W_\mu^\sigma(p_1+k_1+2,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1+2,\beta_1)\,i_\mu^\sigma(q_2+k_2^{max}-k_2,\beta_2) \\
+ W_\mu^\sigma(p_1+k_1+2,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1,\beta_1)\,i_\mu^\sigma(q_2+k_2^{max}-k_2+2,\beta_2) \\
- W_\mu^\sigma(p_1+k_1+2,p_2+k_2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1+2,\beta_1)\,i_\mu^\sigma(q_2+k_2^{max}-k_2+2,\beta_2) \\
- W_\mu^\sigma(p_1+k_1,p_2+k_2+2,\alpha_1,\alpha_2)\,i_\mu^\sigma(q_1+k_1^{max}-k_1,\beta_1)\,i_\mu^\sigma(q_2+k_2^{max}-k_2,\beta_2)
\end{aligned}
$$

$$
\begin{aligned}
&+ W^{\sigma}_{\mu}(p_1+k_1, p_2+k_2+2, \alpha_1, \alpha_2)\, i^{\sigma}_{\mu}(q_1+k_1^{max}-k_1+2, \beta_1)\, i^{\sigma}_{\mu}(q_2+k_2^{max}-k_2, \beta_2) \\
&+ W^{\sigma}_{\mu}(p_1+k_1, p_2+k_2+2, \alpha_1, \alpha_2)\, i^{\sigma}_{\mu}(q_1+k_1^{max}-k_1, \beta_1)\, i^{\sigma}_{\mu}(q_2+k_2^{max}-k_2+2, \beta_2) \\
&- W^{\sigma}_{\mu}(p_1+k_1, p_2+k_2+2, \alpha_1, \alpha_2)\, i^{\sigma}_{\mu}(q_1+k_1^{max}-k_1+2, \beta_1)\, i^{\sigma}_{\mu}(q_2+k_2^{max}-k_2+2, \beta_2) \\
&+ W^{\sigma}_{\mu}(p_1+k_1+2, p_2+k_2+2, \alpha_1, \alpha_2)\, i^{\sigma}_{\mu}(q_1+k_1^{max}-k_1, \beta_1)\, i^{\sigma}_{\mu}(q_2+k_2^{max}-k_2, \beta_2) \\
&- W^{\sigma}_{\mu}(p_1+k_1+2, p_2+k_2+2, \alpha_1, \alpha_2)\, i^{\sigma}_{\mu}(q_1+k_1^{max}-k_1+2, \beta_1)\, i^{\sigma}_{\mu}(q_2+k_2^{max}-k_2, \beta_2) \\
&- W^{\sigma}_{\mu}(p_1+k_1+2, p_2+k_2+2, \alpha_1, \alpha_2)\, i^{\sigma}_{\mu}(q_1+k_1^{max}-k_1, \beta_1)\, i^{\sigma}_{\mu}(q_2+k_2^{max}-k_2+2, \beta_2) \\
&+ W^{\sigma}_{\mu}(p_1+k_1+2, p_2+k_2+2, \alpha_1, \alpha_2)\, i^{\sigma}_{\mu}(q_1+k_1^{max}-k_1+2, \beta_1)\, i^{\sigma}_{\mu}(q_2+k_2^{max}-k_2+2, \beta_2)\Big] \\
&+ \Big\{1 \rightarrow 2\Big\}\Big].
\end{aligned}
$$

The last term in the curly brackets denotes an expression analogous to the second sum but corresponding to the factor $e^{-i(\phi_1-\phi_2)}$ in Eq. (4.3.16).

6.2. Appendix B. List of all matrix elements calculated by the program

In the tables below we list all matrix elements which can be calculated by the present version of the program. Some of them are not fully tested yet but are nonetheless included to signal that their calculation will be available in a foreseeable future. Let us begin with the one-electron matrix elements in the following generic form

$$
\int d\mathbf{r}\; \chi^{*}_{n_a l_a m}(\mathbf{r}_a; \zeta_a)\, \hat{X}\, \chi_{n_b l_b m}(\mathbf{r}_b; \zeta_b), \tag{6.2.1}
$$

where $\hat{X}$ is some one-electron operator. The special cases $a = b$, $\zeta_a = \zeta_b$, etc. are included by default unless explicitly stated otherwise. All one-electron matrix elements are listed in Table 6.2.1. Non-canonical STOs are not considered here. Geometric derivatives of some of the integrals are also available but are not indicated in Table 6.2.1.

Table 6.2.1: List of all one-electron matrix elements in the form (6.2.1) calculated by the program.

name	operator	miscellaneous comments
overlap	$\hat{1}$	—
kinetic energy	$-\frac{1}{2}\nabla^2$	—
nuclear attraction	$-\sum_a \frac{Z_a}{r_a}$	summed over all nuclei
dipole moment	$\mathbf{r}_c = x_c, y_c, z_c$	Cartesian repr. of the operator; centring (c) selected by a keyword
quadruple moment	$\sqrt{\frac{4\pi}{5}}\, r_a^2\, Y_{2m}(\theta_a, \phi_a)$	spherical repr. of the operator, Racah normalisation, centred at the nuclei
octuple moment	$\sqrt{\frac{4\pi}{7}}\, r_a^3\, Y_{3m}(\theta_a, \phi_a)$	same as above
scalar effective core potentials	$U_L^a(r_a) + \sum_{l=0}^{L-1} \sum_{m=-l}^{+l} \lvert lm\rangle_a \times [U_l^a(r_a) - U_L^a(r_a)]\ {}_a\langle lm\rvert$,	for details see Refs. [529–537] or Paper V
DKH-type integrals	$\left(\nabla \sum_a \frac{Z_a}{r_a}\right) \cdot \nabla$	required for DKH [538–542], IOTC [543–545], and other relativistic two-component methods
one-electron Darwin	$2\pi \sum_a Z_a \delta(\mathbf{r}_a)$	—
dipole velocity	$\nabla_\mu = \partial_\mu, \ \ \mu = x, y, z$	Cartesian repr. of the operator

gradient of the potential	$\sum_a Z_a \frac{\mathbf{r}_a}{r_a^3}$	same as above
mass velocity	$\frac{1}{8}\nabla^4$	calculated by using the symmetric (Hermitian) formula
spin-orbit effective core potentials	$\sum_{l=0}^{L-1}\sum_{m=-l}^{+l} \frac{2\,\Delta U_l^a(r_a)}{2l+1} \lvert lm\rangle_a \, \mathbf{l}_a \cdot \mathbf{s}_a \langle lm\rvert$,	for details see Refs. [546–548] or Paper V
core polarisation, vector-type	$\frac{\mathbf{r}_a}{r_a^3}\left(1-e^{-\delta r_a^2}\right)^n$	for details see Refs. [549–551] or Paper V
core polarisation, scalar-type	$\frac{1}{r_a^4}\left(1-e^{-\delta r_a^2}\right)^{2n}$	same as above
angular momentum	$\hat{L}_\mu = i\,(\mathbf{r}\times\nabla)_\mu, \;\; \mu = x,y,z$	Cartesian repr. of the operator
HCS nuclear model	Eq. (4.2.1)	see Sec. 4.2.2 for futher details
Gaussian nuclear model	Eq. (4.2.3)	same as above
Fermi nuclear model	Eq. (4.2.7)	same as above

Two-electron matrix elements are defined analogously as in Eq. (6.2.1) but the operator $\hat{X}$ is now a two-electron object and the integral contains four STOs. Table 6.2.2 contains all respective matrix elements which can be routinely calculated at present.

Table 6.2.2: List of all two-electron matrix elements calculated by the program.

name	operator	miscellaneous comments
electron repulsion	$\frac{1}{r_{12}}$	—
two-electron Darwin	$\delta(\mathbf{r}_{12})$	—
orbit-orbit	$\frac{\nabla_1 \cdot \nabla_2}{r_{12}} + \frac{\mathbf{r}_{12} \cdot (\mathbf{r}_{12} \cdot \nabla_2) \nabla_1}{r_{12}^3}$	Gaussian fitting
Araki-Sucher	$\hat{P}\left(r_{12}^{-3}\right) = \lim_{a \to 0} \theta(r_{12} - a)\, r_{12}^{-3} + 4\pi \left(\gamma_E + \ln a\right) \delta(\mathbf{r}_{12})$	Gaussian fitting, see Ref. [552]
total angular momentum	$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$	see the previous table

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